

Basic Notions of Thermodynamics and Quantum Mechanics for Natural Sciences

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Survey of Physical Chemistry

Vassiliy Lubchenko



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Introduction

This book is intended as a semester course on the basic notions of Thermodynamics, Thermochemistry, and Quantum Mechanics for students majoring in Science (other than Chemistry and Physics) and Mathematics. It is appropriate as an introductory text for Chemistry and Physics majors as well.

The student must be comfortable with basic notions of Calculus, including partial derivatives and integration. These will be reviewed only briefly, as part of the exposition. The knowledge of basic notions of probability, differential equations, and Linear Algebra is not required, but will make the going much easier.

Many thanks to Ms. Vy Quach for taking in-class notes for the the course CHEM4373, taught by me at the University of Houston, and typesetting them. These notes form the basis for the present book. The book is part of the University of Houston initiative on Open Educational Resources (OER). The creation of the book was enabled by an award from UH Alternative Textbook Incentive Program. This award and the assistance of Ms. Ariana Santiago are gratefully acknowledged.

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I

Thermodynamics

1.

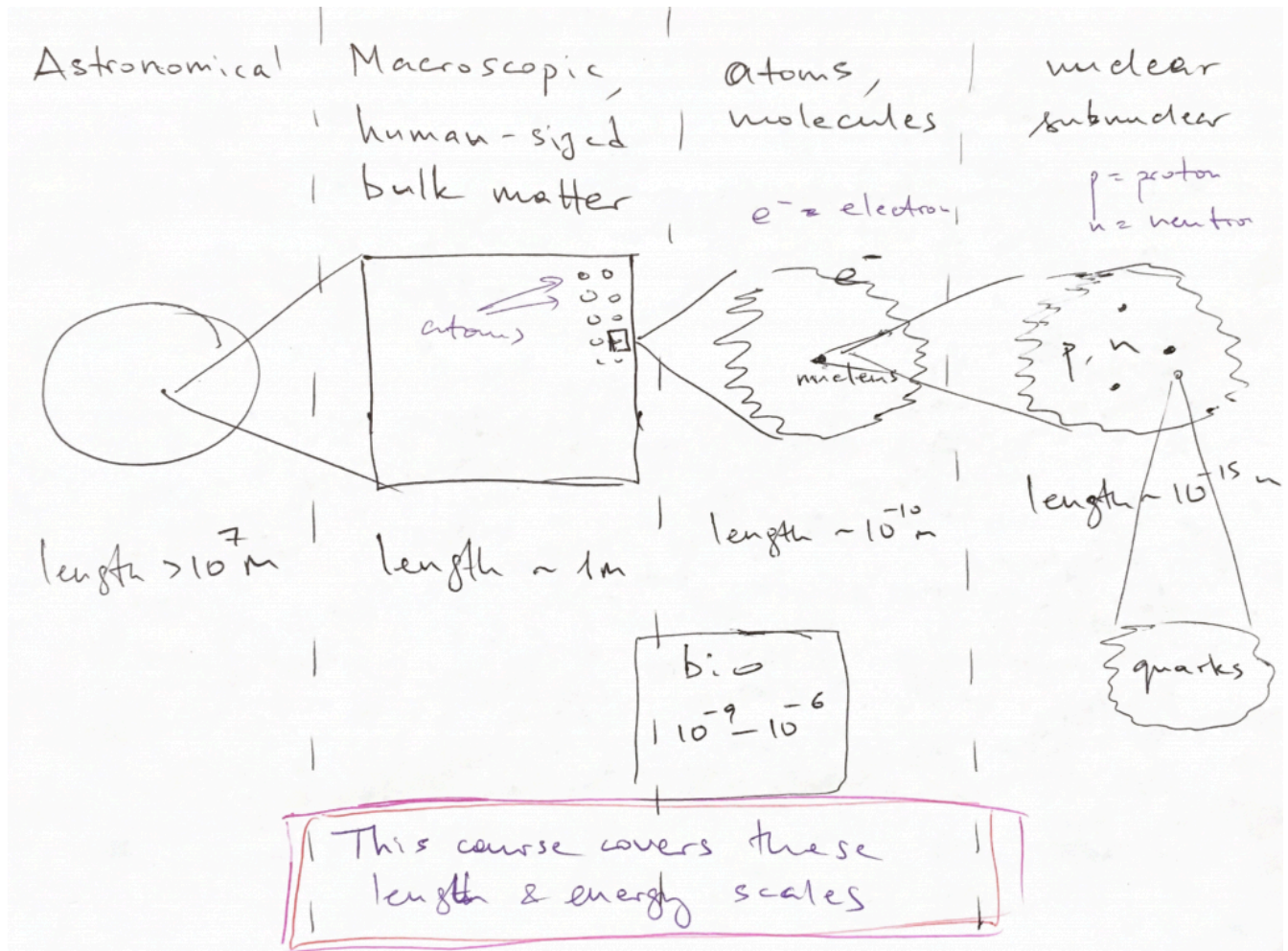
Particulate Organization of Matter. Essential properties of particles.

The world is a story of bound states.

What is a *bound state*? It seems best to give some examples first. A satellite orbiting its planet is a bound state formed as a result of gravitational attraction between the two objects. An atomic nucleus is an example of a bound state formed by nuclear forces, which are a combination of the so called “strong” and “electroweak” interactions, and quantum mechanical effects. Molecules and solids are particularly important for this Course. These are bound states formed as a result of an interplay of electromagnetic forces and quantum mechanical effects.

A common feature shared by those examples is this: A bound state is a union of at least two objects, such that the objects perform concerted, recurrent motions. In other words, these motions are synchronous and are oscillatory, cyclic. The Solar System, galaxies, molecules, solids, atomic nuclei are all examples of bound states. The union could last for just a few cycles or for many many cycles. In the former case, we call the union a weakly bound state, in the latter case a stable (or, more precisely, metastable) bound state. In either case, the breaking of the union, if any, will be a relatively rare event on the time scale of an individual oscillation.

In a great variety of cases of interest, a bound state of two or more objects has a special property: It interacts with the rest of the Universe more weakly than each of constituent parts of the bound state would. For instance, two hydrogen atoms, when combined in a H_2 molecule, are less likely to form a covalent bond with another molecule than a standalone hydrogen atom that has an unpaired electron to share. This may lead to an interesting situation. If it is indeed true that a bound state interacts only weakly with other entities, then the bound states corresponding to this new, weaker energy scale will generally be characterized by a different length scale as well. The new energy scale is smaller, the length scale is larger. This is a very simplified view of things yet it informally illustrates that physical phenomena form a hierarchy, both in terms of length scale and the associated energy scale. There are bound states at each level of the hierarchy: Here is an informal graphic illustrating this hierarchy of bound states, length-wise:



- **$> 10^7 \text{ m}$:** Planets, planetary systems, galaxies, the Universe. At these large scales, the gravity, the weakest force in the Universe, dominates. The effective charge is the mass itself. The other interactions, such as the electromagnetic interactions, are unimportant because the corresponding charges of macroscopic objects, such as planets, are zero.
- **10^{-10} m to 10^0 m :** Atoms/ solids/ liquids/ gases. Electromagnetic forces govern phenomena at these length scale. *These length scales are the subject of this Course.*
- **$< 10^{-15} \text{ m}$:** Nuclear and sub-nuclear phenomena, covered by Nuclear Physics and High Energy Physics. The dominant interactions here are the so called “electro-weak interactions” and the “strong interactions”

Two macroscopic objects ordinarily do not interact electrostatically because their electric charges are zero; they consist of an equal measure of positively and negatively charged particles. There is a remnant of the electrostatic interaction that has to do with the fact that charges comprising an overall neutral system can move while remaining mutually bound; this motion is called “polarization”. The interaction caused by mutually-induced polarization of electrically neutral objects however decays rather quickly with distance. As a result, macroscopic objects interact largely through a much weaker, gravitational force and can be thought of as particles that have only the gravitational charge, i.e., the mass. Similarly, a helium atom consists of two electrons, each charged at -1 (electron charge) and a nucleus charged at $+2$ (electron charges). In addition to being electrically neutral, a helium atom does not have an orbital that can readily accept an electron, nor is it too keen on giving up an electron, for reasons we will discuss later. As a result, a helium atom will not readily form a covalent and/or ionic bond. Instead, they can will interact with the environment via a weaker force.

The physical situations described in the preceding paragraph are relatively clear-cut examples of bound states that act as “particles”, i.e., objects whose internal interactions are significantly stronger than the interaction of the particle with the rest of the world. Conversely, the internal structure of a particle, if any, and at least some of the particle’s properties are only weakly perturbed by the environment. These properties, then, become convenient in discussing particles as standalone entities and, also, as starting points in discussing *collections* of particles. Informally speaking, the existence of properties that are not significantly perturbed by the environment of a particle means that the particle does not completely lose its “individuality” even when it interacts with the environment.

The notions of particles as long-lived bound states is decidedly modern and has resulted from research in Physics and Chemistry over the past two centuries or so. Yet well before the arrival of these modern ideas, people had already recognized that matter consists of bits that seem to be indivisible. The ancient Greeks (Democritus, Leucippus, ~500 BC) spoke of “atoms”, i.e., indivisible units of matter that remain in constant motion, while Lucretius, ~50 BC) discussed the gradual erosion of rocks. These early scholars thus noted that the **mass** and **volume** of macroscopic objects seems to change in *discrete*, even if tiny, units, but not continuously. Later work on electricity (Faraday, 19th century) proved that the **electric charge** also seems to change in discrete bits, namely, $1.6 \cdot 10^{-19}\text{C}$ (C=Coulomb). These three physical properties are, in fact, of prime interest for us in this Course. There is another property, called the **spin**, which is the intrinsic *angular momentum* possessed by small particles such as atoms and molecules, whose existence became apparent upon development of spectroscopy in the 20th century. Let us briefly review these four properties below:

What are some of these properties/descriptors (or “traits”, if you will) that individual particles could possess?

Mass:

A non-vanishing *inertial mass* reflects the property of *inertia*, i.e. the propensity to resist external attempts to change the state of motion of the object. For example, it takes a finite amount of work to force a stationary object to attain a finite velocity. Likewise, it takes an effort to stop a moving object. *Gravitational mass*: the effective charge for the gravitational interaction. Einstein showed that the inertial and gravitational mass are equivalent, which had been known before him but as a purely empirical notion as emphasized by Newton and Hooke, among others.

Volume:

The concept of volume is rather intuitive. Here we will often think of the volume as a quantitative measure of the amount of space occupied by a body or a collection of objects, such as a gas contained within a reservoir of volume V . Another useful application is the *excluded volume*, i.e., the portion of space occupied by a particle and is not accessible to other particles. This is the origin of the so called steric forces (or, excluded volume interaction) in Chemistry.

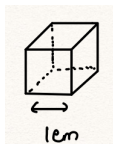
Here we consider a useful example combining the concepts of particle, mass and volume, which deals with the *specific volume* and the related concept of the *volumetric size*.

The numbers of chemically distinct particles (atoms or molecules) that we generally deal with in a chemical or biological context are usually very very large, because those particles are very very small relative to a human. Thus it is often convenient to count those particles in large blocks. By convention, we count particles in blocks called *moles*, each mole containing 6.022×10^{23} particles. The latter number is often called Avogadro’s number:

$$N_A = 6.022 \times 10^{23} \frac{1}{\text{mol}}$$

The numerical value of N_A was chosen specifically so that one mole of hydrogen atoms weighs 1 g.

Q: How many H₂O molecules are contained in 1L of liquid water?



The mass density of liquid water is 1.00 g/cm^3 .

Thus, 1 cm^3 of H_2O weighs $= 1.00 \text{ g} = 1.00 \times 10^{-3} \text{ kg}$

Thus, $1\text{L} = (10 \text{ cm}) \times (10 \text{ cm}) \times (10 \text{ cm}) = 10^{-3} \text{ m}^3$ of liquid water weighs $1.00 \text{ kg} = 1.00 \times 10^3 \text{ g}$.

1 mole of H weighs 1.00 g

1 mole of O weighs 16.0 g

\Rightarrow 1 mole of H_2O weighs 18.00 g .

Thus 1L of liquid water contains

$$\frac{10^3 \text{ g}}{18.0 \text{ g/mol}} = 55.0 \text{ moles} = 55 \times 6.02 \times 10^{23} \text{ particles}$$

Q: What is the specific volume (volume per molecule) of liquid water?

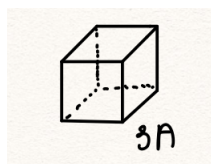
By definition, the specific volume v is found by dividing the total volume V by the particle number N :

$$v = \frac{V}{N}$$

Note the specific volume is the reciprocal of the concentration. Use this formula and the calculations above to check that the specific volume of liquid water is approximately 30 \AA^3 .

Q: What is the volumetric size of a molecule and what is the size of a molecule?

We can use the preceding exercise to evaluate how much “personal space” a single water molecule has for itself, when surrounded by other molecules. For this, we must however assume a specific way the molecules are arranged. In the simplest arrangement, let us assume the molecules are confined to non-overlapping cells of cubic shape, all cells having the same size. By construction, the cells fill (or “tile”) the space,



According to the calculation above, the volume of each of these cubic cells is 30 \AA^3

The lateral size of this cell, or the volumetric size of a water molecule in liquid water is, then $(30 \text{ \AA}^3)^{1/3} \approx 3 \text{ \AA}$.

If we further assume that water molecules are packed tightly (which is true, as we will see later), then the latter length also gives us an idea how large a water molecule actually is. For comparison, the O-H bond length is 1.0 \AA , not bad!

It is necessary to emphasize that the specific volume, i.e., the volume per particle, is a useful measure of the molecular size only in condensed systems, namely, liquids and solids. In sufficiently dilute gases, the specific volume may exceed the molecular volume by an arbitrary amount. The volume of a gas is determined exclusively by the volume of the container!

Bonus Q: Give that the pH of water is 7 at normal conditions, that fraction of liquid water is dissociated at normal conditions?

According to calculations above,

$$[\text{H}_2\text{O}] = 55 \text{ M} \equiv 55 \text{ mol/L}$$

On the other hand, the pH of water is 7 at normal conditions, implying $[\text{H}^+] = 10^{-7} \text{ M}$. Since two protons are freed as a result of dissociating a single water molecule, one gets:

$$\frac{2[\text{H}^+]}{[\text{H}_2\text{O}]} = \frac{10^{-7}\text{M}}{55\text{M}} = 1.8 \times 10^{-9}$$

Electric Charge: Because most bodies are electrically neutral most of the time, we don't deal with the static charge too often. Static electricity does reveal itself, nonetheless, if one rubs certain things against each other, such as the hair and the comb during brushing your hair. Most commonly, we encounter not the charge itself, but the current, which is the flux of charge. For instance, let's estimate the amount of charge q that runs through a typical household appliance in the course of time t . By definition of the electric current, $I = q/t$,

$$q = I \cdot t = \frac{\text{power}}{U} t$$

where U is the voltage and we used the fact that the power is evaluated as the product of the current and voltage. (I've eschewed some non-essential complications due to the current and voltage being alternating, not constant.)

Substituting 100 W for the power, $U = 120$ Volt, and $t = 3600$ sec, we obtain that 3×10^3 C worth of electric charge will flow through a common appliance in hour. For comparison, the amount of charge that passes through a lightning bolt is only 10^2 C or so. Clearly, the lightning is so destructive not so much because of the overall amount of charge, but because of the huge currents that it induces. Conversely, the voltage generated between the comb and the hair during brushing is a couple of kilovolts yet it causes no damage because the currents involved are tiny. This is because the air, unless ionized, does not conduct electricity well. (Air does get ionized inside a lightning rod!)

Spin: The *spin* is yet another word for the *angular momentum*, which is the rotational analog of the momentum of translational motion. By definition, the momentum is the particle's mass m multiplied by its velocity \vec{v} :

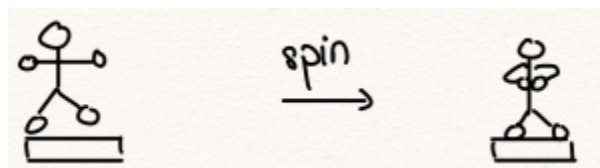
$$\vec{p} = m\vec{v}$$

Likewise, the angular momentum is defined as the moment of inertia I times the angular velocity $\vec{\omega}$:

$$\vec{M} = I\vec{\omega}$$

This formula is less confusing in the scalar form, which only involves the absolute values of the vectorial quantities: $M = I\omega$, where ω is now simply the rate of revolution times 2π .

It turns out, empirically, that both momentum and orbital momentum are conserved (i.e. do not change) in the absence of interaction with the rest of the world. The conservation of angular momentum is vividly demonstrated by tucking in one's arms while spinning on a rotating platform, which then results in an increase in the spinning rate:



This can be quantified by noting the definition of the angular momentum for a compound object consisting of point-like objects:

$$I = \sum_j m_j r_j^2$$

where m_j is the mass of object j and r_j is the distance of object j from the axis of rotation. Clearly, as one tucks one's arms in, the moment of inertia decreases. Since the product $I\omega$ must remain constant, because of the conservation of angular momentum, the rotation rate ω must increase after the spinning person tucks in his/her arms.

It turns out that, like the electric charge, the orbital momentum changes in discrete bits as well, which is one of the most fundamental facts of Nature.

Now that we have introduced the concept of a particle, we are ready to state the main goal of the first part of this course, devoted to Thermodynamics. Here we will use basic notions of mechanics and statistics

to connect phenomena taking place at the molecular scale with macroscopic thermal phenomena. In the second part of the course, Quantum Mechanics, we will ask about how those bound states we call atoms and molecules come about in the first place.

2.

Review of Mechanics and Some Essential Conservation Laws

Mechanics, arguably the first successful branch of modern Physics, deals with the motions and interactions of tangible objects, or “bodies”. By “interactions”, I literally mean actions like “pushing” and “pulling”, etc. (In fact the word “physics” and the word “push” are cognates.) By “tangible”, I mean everyday objects or things like planets and stars, or moving parts of a mechanism, or even animate objects. These are things that we can see and whose motion we can sense or detect without necessarily causing significant changes to their motion. For instance, we can use photo finish to detect who finished a race first, knowing that the light reflected off the athletes bodies—it is the light that we actually detect!—does not affect the motion or the performance of the athletes. Other types of systems, such as gases or light waves, do not seem to be easily described by standard mechanics, for reasons that will become more clear in the Quantum Mechanics part of the Course. For now, we only note that although we evidently interact with things like air or light, it may not be all that clear how to begin describing the interaction because we can’t even see air or light other than that in the visible range. In contrast, the notion of a particle we discussed previously fits perfectly with the setup of Mechanics, which starts with standalone bodies, all of which have well defined mass, shape, and, possibly, a variety of charges, and *then* consider how interactions between the bodies affect their motion. Mechanics considers the mass and shape, and various charges, if any, as immutable. (Things become a bit more complicated at very high speeds, but the complication is not of principal significance.)

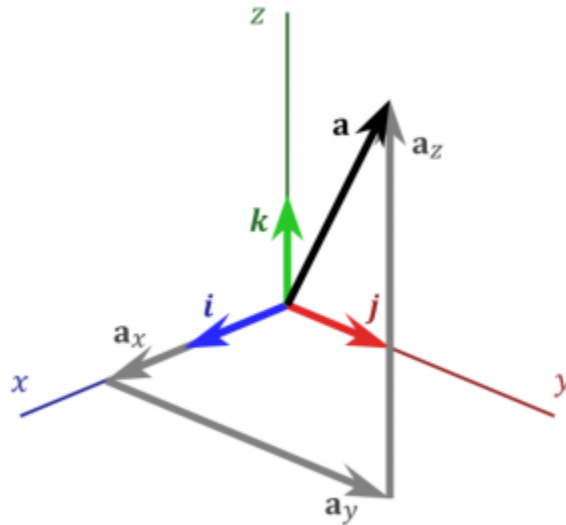
Last but not least, what did I mean by “successful” in the beginning of this discussion? By “successful” I meant the ability of Mechanics to quantitatively predict the future, even if in a limited sense: If we know the laws of interaction and we know the initial coordinates and velocities of the particles involved, we can predict how and where the particles will be moving subsequently, and thus solve many problems of practical interest, such as finding the trajectory of a projectile or an airplane *by doing a calculation*. So, what are the quantities that we aim to predict using Mechanics? We aim to predict where the particle will be at a time t and how fast it will be moving. The location is obviously important, but the velocity is important, too: Being hit by an object moving at 1 cm/sec and 1 m/sec will feel very different! We specify the particle’s location by the vector \vec{r} , whose three components x , y , and z . The velocity is the rate of change of all three components:

$$\begin{aligned}v_x &= dx/dt \\v_y &= dy/dt \\(1) \quad v_z &= dz/dt\end{aligned}$$

which can be economically written down as a single, vectorial equation:

$$(2) \quad \vec{v} = \frac{d\vec{r}}{dt}$$

Indeed, recall that any 3D vector can be presented as a sum of three vectors pointing, respectively, along the coordinate axes, as in the Figure below: (Picture by [User:Acidx](#), [CC BY-SA 4.0](#), [Link](#)):



Those three vectors correspond, respectively, to the motion along the three axes.

It will often be convenient to use a shorthand for the time derivative, namely put a dot above the differentiated quantity. And so, for instance, one can write down the expression for the acceleration \vec{a} , or the rate of change of the velocity, in a variety of equivalent ways:

$$(3) \quad \vec{a} \equiv \frac{d\vec{v}}{dt} \equiv \dot{\vec{v}} = \frac{d^2\vec{r}}{dt^2} \equiv \ddot{\vec{r}}$$

Note that astronomers and navigators had been predicting the motion of celestial bodies for thousands of years before the development of Mechanics, using the regularities of empirical data on the motion of stars and planets. Their assumption was that the observed trends would continue in the future. The breakthrough brought by the modern science is that now we can often predict things in the future without reference to the prior history. Instead, we use laws of physics to write down and solve equations that require, as input, only the configuration of the system at the initial moment, not the prior history. In those cases when the knowledge of history is in fact needed, the equations tell us so. When we deal with very many particles, things can get complicated yet we can still make predictions about some *average* properties of the system, which is the formal essence of Thermodynamics.

The way I wish to review some basic notions of Mechanics here is decidedly modern and probably not the way Newton or Hooke would have done it.

Momentum: The most basic object in the theory is the momentum. The momentum \vec{p} of a particle is defined as product of particle's mass m and velocity \vec{v} :

$$(4) \quad \vec{p} = m\vec{v}$$

Whenever possible, we will use 1D motion for mathematical illustrations, in which case one can get away without using the vector notation:

$$(5) \quad p = mv$$

with the understanding that the quantities p and v can be either positive or negative, the positive sign corresponding to rightward motion, the negative sign corresponding to leftward motion.

For a collection of particles, the total momentum is defined as the sum over the individual particles:

$$\vec{P} = \sum_i \vec{p}_i$$

The basic utility of the momentum comes from the empirical fact that the total momentum of a collection of particles, interacting or not, is conserved (i.e. remains fixed) in the absence of external forces. Furthermore, when a non-vanishing force is present, denote it with f , then the momentum changes at the rate equal to the force itself:

$$(6) \quad \dot{\vec{p}} \equiv \frac{d\vec{p}}{dt} = \vec{f}$$

or

$$(7) \quad \dot{p} = f$$

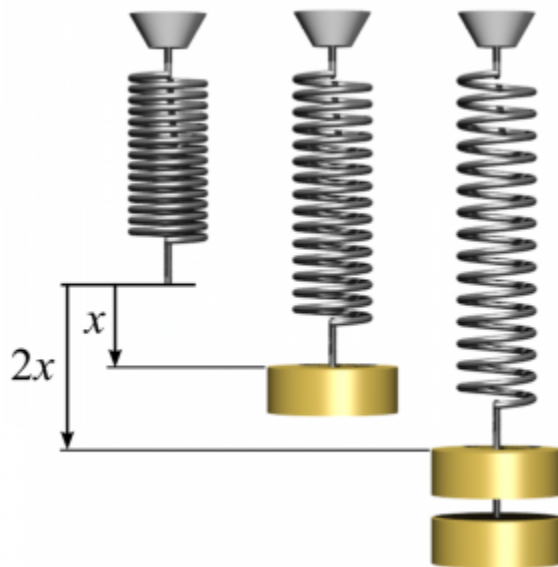
in 1D. Eq. (6) (and Eq. (7)) is a mathematical statement of Newton's 2nd law of Mechanics. In view of Eq. (4), Newton's 2nd law can be also written explicitly as a differential equation for the velocity or the coordinate:

$$m\dot{v} = f$$

$$(8) \quad m\ddot{x} = f$$

The momentum may seem like a rather abstract notion. It is indeed. Yet it allows one to immediately rationalize some rather concrete phenomena of practical importance. Suppose you are floating leisurely in water next to a stationary object, such as a boat. Your mass is m and the boat's mass is M . Imagine next you push yourself away from the boat. Because the total momentum of the you+boat system should remain constant and, hence, equal to its initial value of zero, it must be true that after you are done pushing, the ratio of the boat's velocity to yours should be equal to m/M . ($0 = mv_{\text{you}} + Mv_{\text{boat}} \Rightarrow v_{\text{boat}}/v_{\text{you}} = -m/M$.) That is, the heavier the boat, the more slowly it will be moving at the end of the interaction. In other words, a heavier object exhibits more inertia. I'm sure you can come up with good examples from sports like football, basketball, wrestling, etc. As you may imagine, molecules will follow exactly the same trend when bouncing off one another.

In a great variety of important applications, the force depends on the coordinate of the particle. For instance, for a spring stretched or contracted by the amount x off its equilibrium length:



(Picture by Svjo – Own work, [CC BY-SA 3.0, Link](#))

the restoring force is proportional to the displacement itself, i.e., the famous Hooke's Law:

$$(9) \quad f = -kx$$

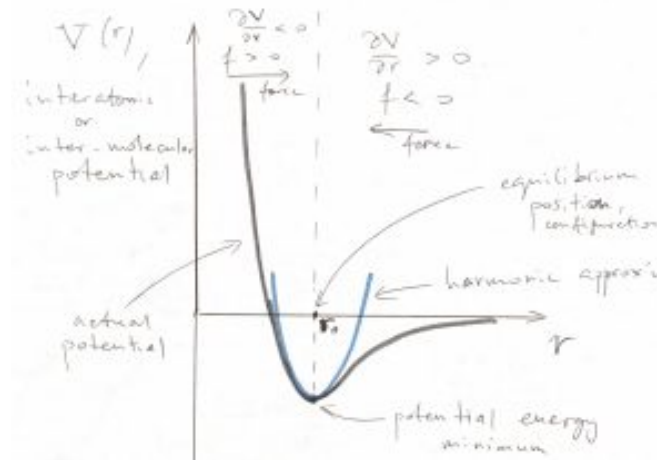
where the positive quantity k is called the spring constant. When the force depends exclusively on the coordinate, it will be often very convenient to work not with the force itself but with a related function called the potential of the force, also referred to as the *potential energy* $V(x)$. In 1D, the potential is defined as any function whose spatial derivative is equal to the force:

$$(10) \quad f = -\frac{dV}{dx}$$

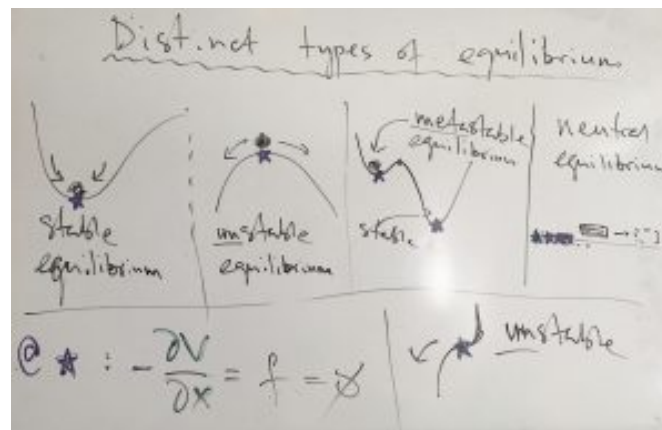
And so, the potential corresponding to the restoring force of a spring from Eq. (9) is a simple parabola:

$$(11) \quad V(x) = \frac{kx^2}{2}$$

This simple parabolic potential is often called the *harmonic* potential, while the corresponding degree of freedom (the coordinate x , in this case) is often referred to as the *harmonic oscillator*. The “oscillations” will be discussed later in this Chapter. It is instructive to sketch the potential energy (11). It is a parabola with positive curvature, much like a tea cup with its bottom down. It is easy to check, using Eq. (10) that the force to this potential is always restoring, i.e., it pushed the object toward the equilibrium point, where $f = 0$. A great advantage of working with potentials, as opposed to forces, is that this framework immediately appeals to our intuitive sense that things subjected to gravity tend to move to lower places. For low-magnitude vibrations, the harmonic potential from Eq. (11) is often a good approximation to other types of potentials, such as the typical potential of inter-molecular or inter-atomic forces:



Though more complicated than the harmonic potential (11), this typical intermolecular potential still has a unique stable minimum. Generally, however, there are other types of equilibrium, where by equilibrium we mean a vanishing force, $f = 0$. In most cases of practical interest, this means the corresponding potential has a stationary point there: $dV/dx = 0$, by Eq. (10).



In the case of unstable equilibrium, there is no restoring force for a particle pushed off the maximum; on the contrary the emerged force will push the particle further away from the equilibrium point. When equilibrium is metastable, the system does exhibit a restoring force but only within a finite range of the coordinate. Neutral equilibrium means no force altogether, at any location. We will learn in this class that a variety of quantities, ranging from a bond length to the volume of a macroscopic system often can be thought of as degrees of freedom that are subject to a potential energy like those depicted above.

In spatial dimensions higher than one, instead of the relatively simple (10) one would have $f_x = -\partial V/\partial x$

, $f_y = -\partial V/\partial y$, etc. To avoid confusion, we note that in 1D, it is always possible to find a potential of the force for any force that depends exclusively on the coordinate, see Eq. (21) below, but this is not necessarily so in spatial dimensions 2 and higher. In any event, because the derivative of a constant vanishes, adding a constant to the potential does not modify the value of the force. If a force does allow for a potential, the force is called *conservative*, for reasons that will become clear shortly.

An important example of a reaction force that depends exclusively on the velocity is the force of friction such as that due to a viscous drag:

$$(12) \quad \vec{f} = -\zeta \vec{v}$$

where we have defined a new, positive quantity ζ , which is called the friction (or damping) coefficient. This friction force acts in the direction exactly opposite of the velocity.

Let us now introduce another, extremely important quantity called the **kinetic energy**. The kinetic energy for a single object is defined as follows:

$$(13) \quad E_{\text{kin}} = \frac{mv^2}{2}$$

For a collection of point masses, it is given by the expression

$$(14) \quad E_{\text{kin}}^{(\text{total})} = \sum_j \frac{m_j v_j^2}{2}$$

This expression will resurface in due time as the energy of the ideal gas.

The kinetic energy—and any type of energy for that matter—is admittedly a very artificial concept. One might even say it is a contrived concept. Yet it is remarkably useful. Indeed, let's consider the sum of the kinetic and potential energy, call it the energy:

$$(15) \quad E = \frac{mv^2}{2} + V(x)$$

Let us now compute the full time derivative of this quantity, using the chain rule of differentiation:

$$(16) \quad \frac{dE}{dt} = \frac{d}{dt} \left[\frac{mv^2}{2} + V(x) \right] = m v \frac{dv}{dt} + \frac{dV}{dx} \frac{dx}{dt} = v \left(m \frac{dv}{dt} + \frac{dV}{dx} \right)$$

where we used that $dx/dt = v$ is the velocity, Eq. (2).

But, according to Newton's second law, Eq. (8) and the relation (10),

$$(17) \quad m \frac{dv}{dt} = f = -\frac{\partial V}{\partial x}$$

Thus,

$$(18) \quad \dot{E} = 0 \Rightarrow E = \text{const}$$

Thus we obtain that if the motion of a body is subject to a conservative force, the energy of this body is conserved, that is, remains constant over time. This is the reason why forces of the type (10) are called conservative. Because of energy conservation, an increase in the potential energy should be accompanied by a decrease in the kinetic energy, the two exactly compensating each other.

In contrast with conservative forces, forces of the type (12) are dissipative, because they always cause the energy of the body to decrease, see below. The effect of inter-molecular collisions is often well approximated with such frictional forces. The energy is taken away from the body in question and passed on to those molecules that collide with the body. The total energy is however conserved.

As a consequence, **the total energy of a collection of bodies that is isolated from the rest of the world remains constant over time.** Conversely, if the energy of the system does happen to change, we know that an act of

interaction with the environment must have occurred. This notion will come in handy later on when we discuss statistics of distinct microscopic configurations of various systems of interest.

FYI: Momentum and energy conservation are intrinsically related (which was revealed by Einstein's theory of relativity) and can be interpreted as the invariance of physical laws with respect to space and time translation, respectively. (This is the gist of a famous theorem due to Emmy Noether, https://en.wikipedia.org/wiki/Emmy_Noether). In other words, the laws of physics are the same everywhere in space and do not change over time either.

The apparent conservation of momentum and energy is of great value in a number of ways. In addition to revealing deep properties of space and time, they often make it easier for us to solve problems of interest, as we have already seen in the boat example earlier.

Let us consider the energy of a particle subject to a conservative force, see Eq. (15) in which case the energy stays constant. Equating the energy values at two distinct times yields:

$$(19) \quad \frac{m v_1^2}{2} + V(x_1) = \frac{m v_2^2}{2} + V(x_2)$$

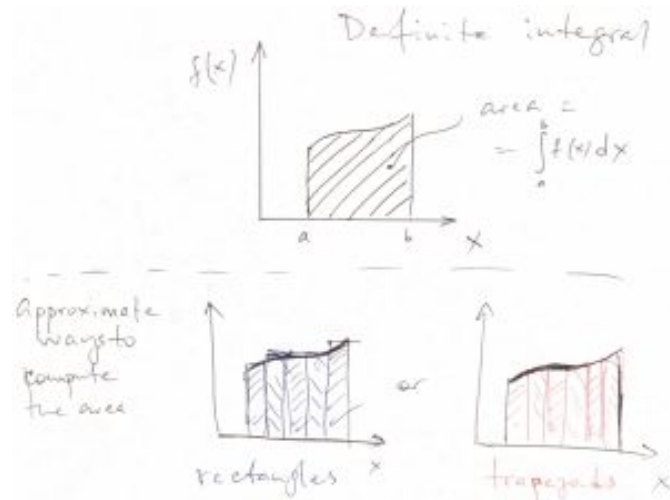
Thus one gets that the increment of the kinetic energy is the negative of the increment of the potential energy:

$$(20) \quad \Delta \frac{mv^2}{2} \equiv \left. \frac{mv^2}{2} \right|_1^2 \equiv \frac{mv_2^2}{2} - \frac{mv_1^2}{2} = -V(x_2) + V(x_1) \equiv -\Delta V(x)$$

In turn, the potential energy increment can be presented as the integral of the force, with the minus sign:

$$(21) \quad \Delta V(x) \equiv V(x_2) - V(x_1) = \int_1^2 dV(x) = \int_1^2 \frac{dV}{dx} dx = - \int_1^2 f dx$$

Note that this equation represents the reciprocal operation to that in Eq. (10). The figure below graphically reviews the notion of the definite integral and two specific approximations used to compute such an integral:



The second approximation, where we compute the total area of the shape by adding together the areas of the trapezoids, can be used to show rather explicitly that the increment of a function over a finite change in the argument is simply the integral of the derivative of that function:

$$(22) \quad W_{1 \rightarrow 2} = \int_1^2 f dx$$

According to Eq. (21), the work performed by a conservative force acting on an object is simply equal to the negative increment in the potential accompanying the displacement:

$$(23) \quad W_{1 \rightarrow 2} = -\Delta V(x) \text{ , if the force is conservative: } f = -\frac{dV}{dx}$$

Eqs. (20) and (21) thus yield for the change in the kinetic energy of an object acted upon by conservative forces exclusively:

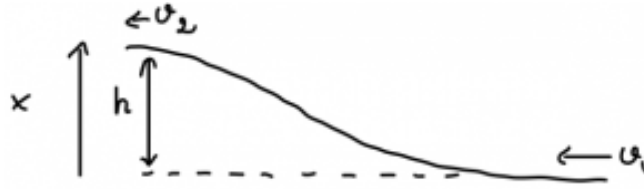
$$(24) \quad \Delta \frac{mv^2}{2} = -\Delta V(x) = W_{1 \rightarrow 2}$$

- **Positive work by external force** → **increase in internal energy**
- **Negative work by external force** → **decrease in internal energy**

Some examples of practical applications of the law of conservation of energy

Our **first example** will be for the simple yet incredibly important case of a spatially uniform (i.e. “same everywhere”) force. This is a good approximation for the force of gravity for distances from the ground that are much smaller than the Earth’s size. A body of mass m is subject to a force of gravity $-mg$, where the minus sign indicates that the force is downward. (The coordinate axis we use to specify the displacement is oriented

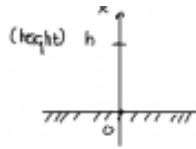
upward.) By Eq. (21), the potential difference between two points at height x_2 and x_1 respectively is, then, $V(x_2) - V(x_1) = mg(x_2 - x_1)$. Thus, for instance, an object that moves inertially uphill will be losing its kinetic energy as its height increases:



$$(25) \quad \frac{m v_2^2}{2} - \frac{m v_1^2}{2} = -mgh$$

This can be used to immediately deduce how high a projectile will go, if its vertical velocity is v . Setting $v_2 = 0$ and $v_1 = v$ in the equation above yields $h = v^2/2g$. Analogously, an object dropped from height h will reach the velocity $\sqrt{2gh}$ just before it hits the ground. Note we didn't have to solve any differential equations to obtain these estimates. Pretty convenient, isn't it?

We can use these ideas to understand why solvated protein molecules do not sink to the bottom of the container even though protein mass density is about 1.2 g/cm^3 , which is greater than that density of liquid water. The typical energy of an individual protein molecule is $k_B T$ (to be derived later) where the Boltzmann constant k_B is numerically $1.38 \times 10^{-23} \text{ J/K}$ and T is temperature. This typical energy scale is to be compared with mgh , where h is the height of the flask. One can easily check that the variation of the potential energy, as a protein molecule traverses vertically the flask, are much smaller than the typical energy of the molecule: $mgh \ll k_B T$. In other words, the potential energy variations in this case are only a tiny perturbation implying that the protein density variations due to the field of gravity would be small, too. Conversely, one can estimate the largest achievable height for a particle possessing a typical thermal energy, which, then, allows one to estimate the height of the atmosphere:



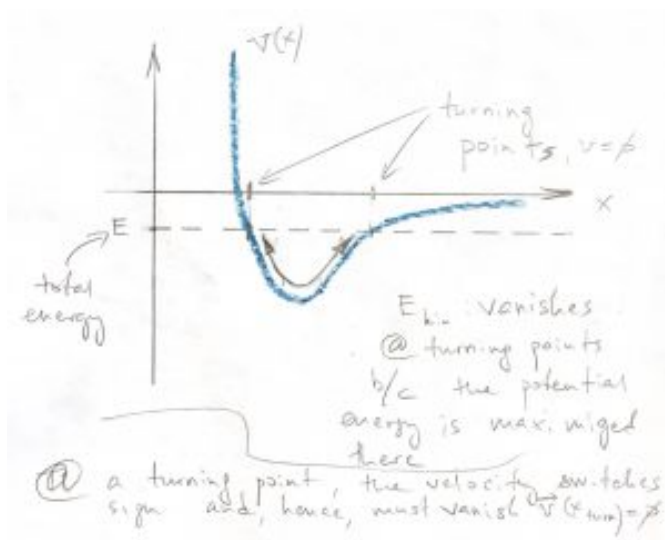
achievable height h estimated as
 $mgh \sim k_B T$

Now, even if energy conservation does not absolve us from having to solve a differential equation, it often helps to make it easier, which brings us to our **second example**, viz., 1D motion subject to a conservative force. Newton's 2nd law implies the following 2nd order differential equation for the motion:

$$(26) \quad m \frac{d^2 x}{dt^2} = -\frac{dV}{dx}$$

which is generally hard to solve. Energy conservation allows one to reduce this problem to a 1st order differential equation. Indeed, the total energy is fixed and, furthermore, equal to the value of the potential energy at any of the turning points x_{turning} . This is because at a turning point, the velocity switches sign and, thus, must vanish. As a result, the kinetic energy at turning points is zero (in 1D). Therefore,

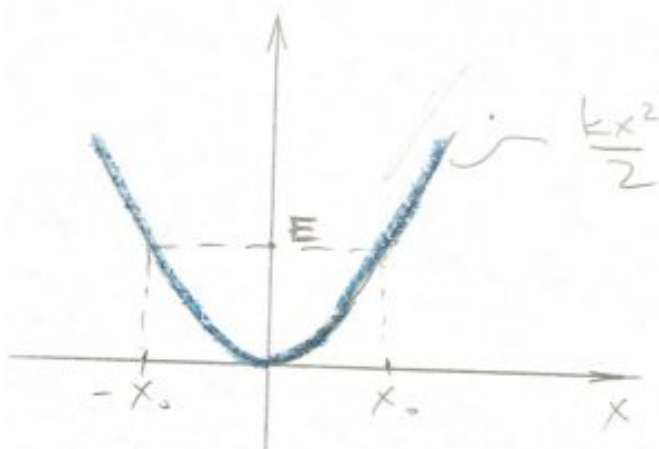
$$(27) \quad \frac{mv^2}{2} + V(x) = \text{constant} = V(x_{\text{turning}})$$



For the harmonic oscillator, this leads to:

$$(28) \quad \frac{dx}{\sqrt{x_0^2 - x^2}} = (2k/m)^{1/2} dt$$

because the turning points are x_0 and $(-x_0)$.



The equation above is straightforwardly integrated using standard Tables of Integrals. For instance, if we choose the integration constant so that the particle is at the r.h.s. turning point at time zero, $x(t=0) = x_0$, then one obtains:

$$(29) \quad x = x_0 \cos(\omega t)$$

where the quantity

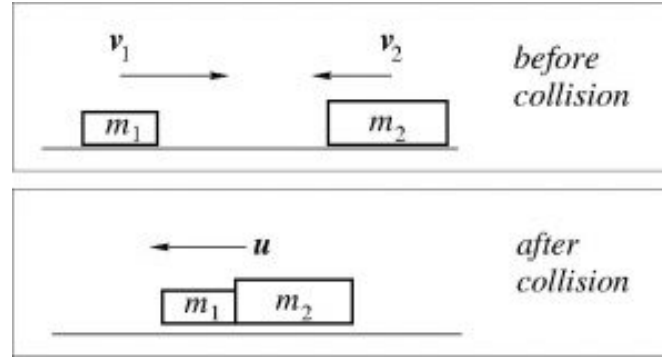
$$(30) \quad \omega \equiv \sqrt{k/m}$$

is the oscillator's circular frequency. (Can you use the just obtained solution for $x(t)$ to check that the total energy of harmonic oscillator is conserved?) Note the harmonic oscillator is a unique dynamical system in that its period of oscillation does not depend on the magnitude of the motion!

Two examples of combined applications of the laws of conservation of energy and of conservation of momentum

Two final examples involve collisions of objects, which will come in handy soon, when we discuss molecular scale processes.

Imagine two moving objects that collide, stick together upon the collision, and then continue motion as a compound object:



The collision leads to very complicated processes inside the bodies, such as shock waves, heating and what not, yet the fact of momentum conservation allows us to evaluate the velocity of the compound object without having to solve any equations:

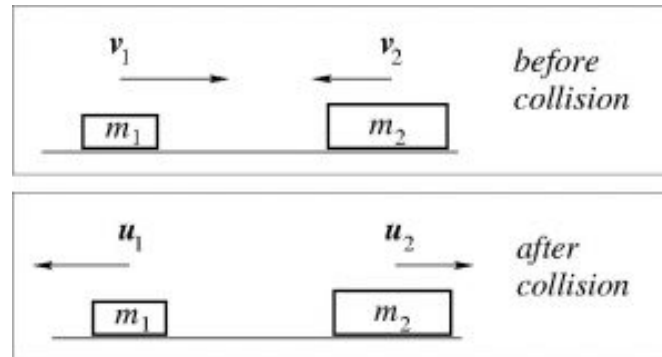
$$m_1 v_1 + m_2 v_2 = (m_1 + m_2) u$$

We can now evaluate the change in the kinetic energy:

$$(31) \quad \frac{(m_1 + m_2)u^2}{2} - \left(\frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2} \right) = -\frac{(m_1 m_2)(v_1 - v_2)^2}{2(m_1 + m_2)} \leq 0$$

The kinetic energy clearly decreases as a result of the collision, since in order for the two objects to collide, their velocity must be different. Where did the missing energy go? Since there are no external forces involved, this energy must have gone on to heat up the compound object! A collision where any amount energy has been dissipated into heat is called *inelastic*.

To finish, we will consider the opposite extreme limit of a purely elastic collision:



In this case, the momentum and energy conservation yield two equations:

$$\begin{aligned} m_1 v_1 + m_2 v_2 &= m_1 u_1 + m_2 u_2 \\ \frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2} &= \frac{m_1 u_1^2}{2} + \frac{m_2 u_2^2}{2} \end{aligned}$$

which can be solved for two unknowns, namely, the velocities of the objects after the collision is over:

$$(32) \quad u_1 = -v_1 + 2 \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

$$(33) \quad u_2 = -v_2 + 2 \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

FYI: The above solution could have been obtained even in a simpler fashion by transferring to the reference

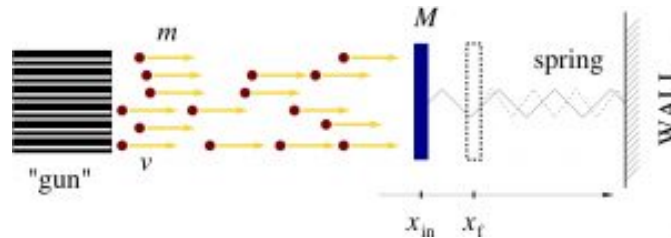
frame moving with the center of mass, $v_{\text{CM}} = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$, and then noting that in that frame, the position of the center of mass is immutable, as if it were an infinitely heavy wall. Since no energy is dissipated, each object will bounce off that “wall” with the velocity equal in magnitude to the incoming velocity, but opposite in sign. Transferring back to the original reference frame yields, then, Eqs. (32) and (33). Working in the reference frame moving with the center of mass also makes it clear that for collisions that are not completely elastic the particles will recoil less. Most dissipation occurs when the bodies don’t bounce at all, i.e., when they end up stuck together. This is exactly the situation we considered in the preceding example.

3.

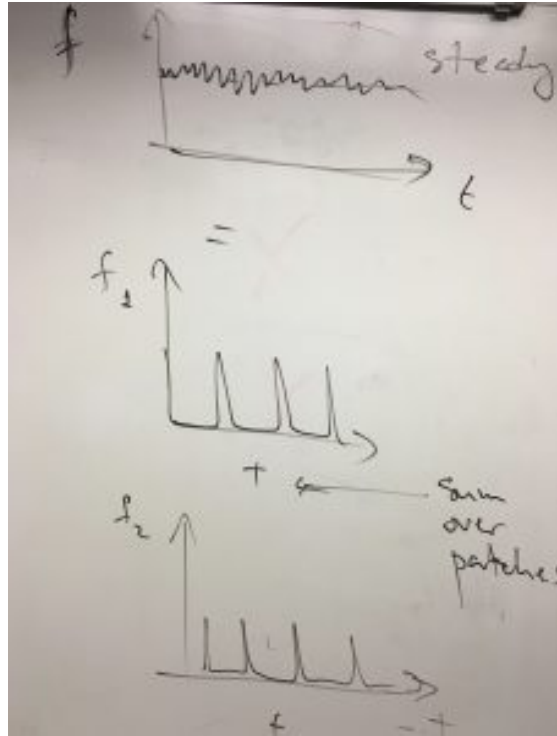
The molecular origin of hydrostatic pressure and the notion of flux

Here we discuss how the pressure in a gas or liquid comes about at the molecular level and derive an expression for pressure, which is a macroscopic concept, through quantities pertaining to individual molecules. Pressure is a combined result of many molecules hitting the wall of the container. Despite the intermittent character of the molecular collisions, pressure is steady because the effective force exerted by those colliding molecules on the container's walls is averaged over a substantial area and over times that greatly exceed the duration of an individual collision.

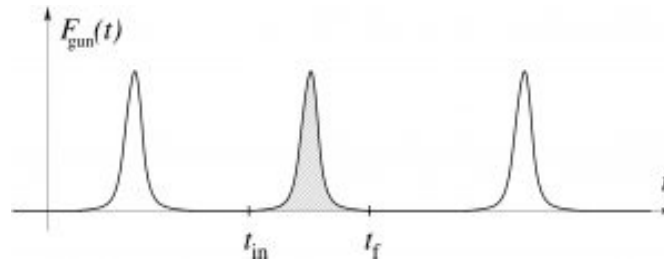
Consider first an idealized setup where we have a steady stream of particles coming out of a source and hitting a heavy shield attached to a stationary wall. The particles each have mass m , velocity v , while the concentration of the particles in the beam is n :



For now, we are interested in a situation where the interactions between the particles are sufficiently weak so that their motions are only weakly correlated, if at all. For the same reason, we will regard the recoiled particles as not interfering in any way with the incoming particles. This argument will eventually lead us to what one calls *the ideal gas*. The force fluctuates wildly around some average value, as time goes by, and is very messy. Since the individual collisions are uncorrelated, it is convenient to separately consider small patches of the shield such that distinct collisions with each such patch do not overlap temporally. (The forces acting on the distinct patches will be added together at the end of the day.)



Each of these partial contributions is a temporal sequence of disparate peaks corresponding to individual collisions:



For an individual collision, the particle just begins to touch the shield at time t_{in} and stops touching it at time t_f , while the force peaks out somewhere in-between.

We are dealing here with a force that rapidly changes in time. It spikes during a collision but could be very small at other times. Because the shield is heavy, it will *not* experience correspondingly rapid fluctuations in its velocity, acceleration, or coordinate. Rather, it will experience a force *averaged* over a large number of consecutive collisions. Evaluation of this averaged force is, then, a good starting point for the argument, which can be systematically improved upon by including into the treatment deviations of the instantaneous value of the force from its average value.

Let us estimate the time-averaged force $\langle f \rangle_t$, where the angular brackets denote averaging over time and, consequently, over the collisions. First we break up a sufficiently long time interval $[0, t]$ into many very short intervals Δt_i such that the force can be regarded as constant over each individual interval. Denote this constant force with f_i . The averaging is, then, reduced to the following *weighted average*:

$$(1) \quad \langle f \rangle = \sum_i \frac{\Delta t_i}{t} f_i$$

The averaging above is completely analogous to evaluating, for instance, the average grade in a class where, say, 30% of the students received an A, 50% students received a B, and 20% percent received a C, and so the average grade is $0.30 \times 4 + 0.50 \times 3 + 0.20 \times 2 = 3.1$. The $\Delta t_i/t$ ratio plays the role of the weight of the interval i . Note the weights add up to 1, as they should:

$$(2) \quad \sum_i \frac{\Delta t_i}{t} = \frac{1}{t} \sum_i \Delta t_i = \frac{1}{t} t = 1$$

(Note also that in contrast with the class grade example, here two distinct intervals do not have to exhibit distinct values of the force f_i .)

A digression on statistics: In case you forgot how weighted averages come about, it may be worthwhile to review this in some detail. Suppose you have sampled (or measured) a distributed quantity x for a total number of N times. It is often useful to determine the average of this quantity over the sampled data:

$$(3) \quad \langle x \rangle \equiv \frac{1}{N} \sum_{\alpha=1}^N x_{\alpha}.$$

Suppose the quantity x can assume any value from an interval $[x_{\min}, x_{\max}]$. We may conveniently subdivide the interval into M small sub-intervals of length Δx , so that

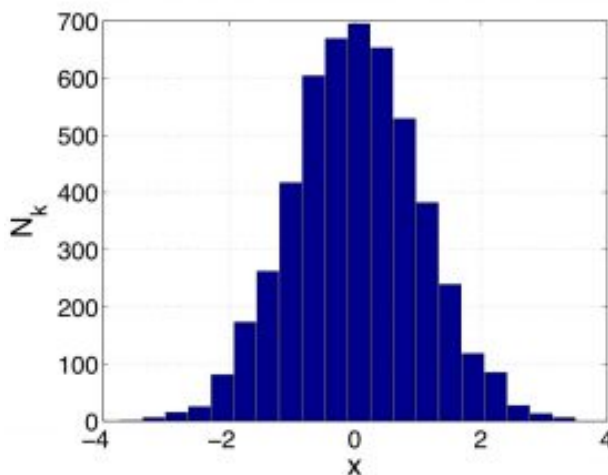
$$(4) \quad \Delta x = \frac{x_{\max} - x_{\min}}{M}.$$

Let us label each sub-interval, or “bin”, by integers 1 through M . Bin k corresponds to the data range $x_{\alpha} \in [x_k, x_{k+1}]$. Let us now break up the sum in Eq. (3) into contributions from the distinct bins:

$$(5) \quad \langle x \rangle = \frac{1}{N} \sum_{k=1}^M \sum_{\text{over bin } k} x_{\alpha}$$

To avoid confusion, we label the original data using the Greek indices, while the bins are labeled with Latin indices.

Suppose there are N_k data in bin k . One should think of N_k as the height of the bar on a histogram where the width of the bar is the quantity Δx itself, such as the one below:



We can conveniently rewrite the equation above as

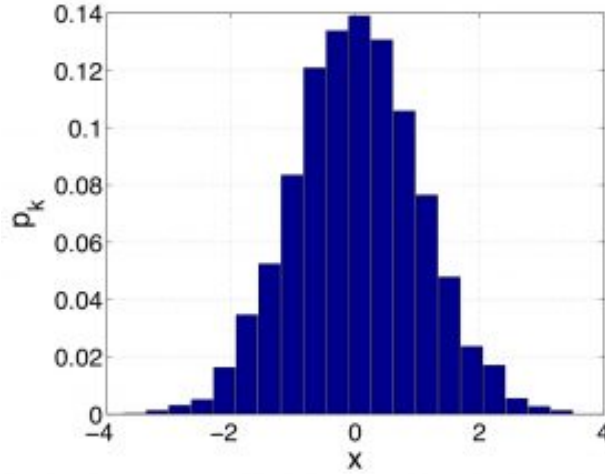
$$(6) \quad \langle x \rangle = \frac{1}{N} \sum_{k=1}^M N_k \frac{1}{N_k} \sum_{\text{over bin } k} x_{\alpha} = \frac{1}{N} \sum_{k=1}^M N_k x_k = \sum_{k=1}^M \frac{N_k}{N} x_k$$

where $x_k \equiv \frac{1}{N_k} \sum_{\text{over bin } k} x_{\alpha}$ is the average of the data that falls within bin k . The quantity x_k automatically falls within bin k , too, and can be thought of, approximately as the position of the center of bin k .

This approximation becomes exact in the limit $\Delta x \rightarrow 0$. One may define the statistical weight of bin k :

$$(7) \quad p_k \equiv \frac{N_k}{N}$$

The weights corresponding to the histogram above are shown below:



These weights obviously add up to unity:

$$(8) \quad \sum_{k=1}^M p_k = \frac{1}{N} \sum_{k=1}^M N_k = \frac{1}{N} N = 1$$

c.f. Eq. (2). With the so defined weights p_k , one can now rewrite the average in Eq. (6) in a way that does not explicitly refer to the total size of the data set, but, instead, specifies the fractional amount, or the probability of the outcome x_k , in the total set of all possible outcomes:

$$(9) \quad \langle x \rangle = \sum_{k=1}^M p_k x_k$$

Since the weights p_k describe how the probability of encountering the corresponding value of x , they are often called the *distribution* of the quantity x . **End of digression on statistics**

Now, in the next step, we take $1/t$ out of the sum in Eq. (1) and take the limit $\Delta t_i \rightarrow 0$, which conveniently yields a definite integral:

$$(10) \quad \langle f \rangle = \frac{1}{t} \lim_{\Delta t_i \rightarrow 0} \sum_i f_i \Delta t_i = \frac{1}{t} \int_0^t f(\tau) d\tau$$

We next present the time integral of the force as a sum over distinct peaks corresponding to distinct collisions, in the Figure above. We will use the dummy index k to label distinct collisions:

$$(11) \quad \langle f \rangle = \frac{1}{t} \int_0^t f(\tau) d\tau = \frac{1}{t} \sum_k^{N_c} \int_{t_{in}^k}^{t_f^k} f(\tau) d\tau$$

where N_c is the total number of collisions that occurred over time t . Let us consider an individual integral in

the above sum and express the force through the time derivative of the momentum P of the shield, as afforded by Newton's second law, $f = \frac{dP}{dt} dt$:

$$(12) \quad \int_{t_{\text{in}}}^{t_{\text{f}}} f dt = \int_{t_{\text{in}}}^{t_{\text{f}}} \frac{dP}{dt} dt = \Delta P$$

where Δp is thus the momentum change of the shield resulting from an individual collision. Subsequently, one may rewrite Eq. (13) as

$$(13) \quad \langle f \rangle = \frac{1}{t} \sum_k^{N_c} \Delta P_k = \frac{N_c}{t} \frac{1}{N_c} \sum_k^{N_c} \Delta P_k = \frac{N_c}{t} \langle \Delta P \rangle$$

that is, the average force is proportional to the average amount momentum transferred to the shield during an individual collision. The proportionality constant is the collision number N_c divided by the duration t of the experiment. The momentum change, due to a single collision is easily inferred from the last problem we solved in Chapter 2:

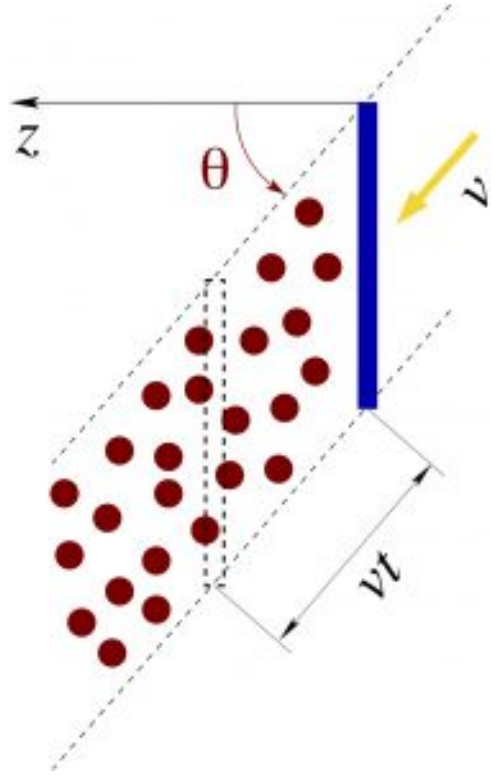
$$(14) \quad \Delta P = \frac{2mM}{m + M} (v - v_{\text{shield}})$$

where v_{shield} is the velocity of the shield just before the collision. We are interested in the steady state result whereby the shield is stationary on the average: $\langle v_{\text{shield}} \rangle = 0$. This leads to

$$(15) \quad \langle \Delta P \rangle = \frac{2mM}{m + M} v$$

Our next step is to determine the ratio $\frac{N_c}{t}$. This ratio is, quite literally, the number of particles crossing a surface per unit time, or the *collision rate*. Evaluation of N_c is done most straightforwardly by going over to the reference frame moving with the particles. In this frame, the particles are stationary, while the shield is moving to the left with the velocity $(-v)$. The number of particles that collided with the shield over time t in the lab reference frame is, then, equal to the number of particles “swept” by the moving shield in the moving frame.

The figure below shows a slightly more general setup, where the shield is tilted so that the normal to its surface is at angle θ to the direction of the particle stream:



If the area of the shield is S , then the volume swept by the shield over time t is equal to

$$(16) \text{ swept volume} = v t S \cos \theta$$

To see this, recall that the volume of a (generally oblique) prism is the area of the base of the prism times the distance between the top and bottom bases. Our “prism” has bases of area S each, while the distance between the two planes containing the respective bases is $v t \cos \theta$.

The number of particles swept is just swept volume times the particle concentration. Thus

$$(17) N_c = n v t S \cos \theta$$

while the rate N_c/t at which particles collide with the shield is

$$(18) \frac{N_c}{t} = n v S \cos \theta$$

This is a useful formula as it allows one to write down a simple result for the **particle flux**, i.e., the number of particles crossing a surface (real or imaginary) per unit time and unit area:

$$(19) \text{ particle flux: } J = \frac{N_c}{t S} = n v \cos \theta$$

Note that the above formula correctly reflects the fact that if the stream is parallel to the surface ($\theta = \pi/2$), the flux vanishes. Note also that the flux is an intensive property: It does not in any way reflect the size of the system, but only reflects its local properties.

Now let us return to our main derivation. In our particle-shield setup, $\theta = 0$. Hence,

$$(20) N_c = n v t S$$

Putting together Eqns. (13), (15), and (20) yields:

$$(21) \langle f \rangle = n \frac{2mM}{m+M} v^2 S$$

As one could have expected, the total force acting on the shield is proportional to the shield's area. It is, then, convenient to define the force per unit area, which we call the *pressure*:

$$(22) \quad p \equiv \frac{f}{S}$$

It is an intensive property, i.e., it does not depend on the system size, which, in this case is the size of the shield. Thus one gets:

$$(23) \quad p = n \frac{2mM}{m+M} v^2$$

Note a rather general expression we can write down in view of Eqs. (13), (19), and (22):

$$(24) \quad p = J \langle \Delta P \rangle$$

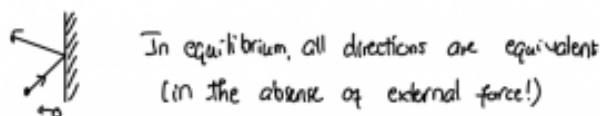
which says that pressure, essentially, amounts to a flux of momentum from the incident particles to the object they are colliding with.

In the important limit of particles being much lighter than the shield, $m \ll M$, Eq. (23) simplifies and, in fact, contains no reference to the properties of the surface that is being bombarded by our particles:

$$(25) \quad p = 2 n m v^2$$

where we used that $mM/(m+M) = m/(1+m/M) \rightarrow m$, as $m/M \rightarrow 0$. Alternatively, one may discuss a pressure on an imaginary, fully stationary surface. In this case, one must assume $M \rightarrow \infty$ for consistency. Either way, we obtain that the pressure due to a steady (even if intermittent) stream particles is the property of the particles and the stream themselves and, thus, is of rather universal nature. The concept of pressure will be prove quite useful indeed.

While fully demonstrating the molecular origin of pressure, Eq. (25) must be generalized a bit before we can apply it to actual gases of particles because in equilibrium gases, the velocities of the particles are distributed. Which means that both the speed and the angle of incidence (this is the angle θ above) are distributed and one must average over those distribution. Setting up the averaging is not too difficult, derivations given in my CHEM4370 notes or any standard texts on Thermodynamics. In short, one should group the incident molecules into streams like the one we have worked with, each stream characterized by a specific value of v and θ and to remember that the momentum transfer to the shield is determined by the component of the particle's velocity along the normal to the shield: $\Delta P \rightarrow \Delta P \cos \theta$. Finally, only a half of all particles is moving toward the shield, while the other half is moving away.



All these complications amount to simply introducing an additional, multiplicative factor $1/6$ into the formula and the necessity to average the speed squared over all particles in the gas:

$$(26) \quad p = \frac{1}{3} n m \langle v^2 \rangle$$

This is the correct formula we will be using to evaluate the pressure in nearly ideal gases, not the “preliminary” formula (25).

Finally, if we are dealing with a mixture of gases, the full pressure will be obtained by summing over the contribution of each component, each contribution given by the above formula with pertinent values of the parameters. In any event, we have done something important today: We have written down a quantitative expression that explicitly connects a macroscopic property of a system with its molecular properties. From a more conceptual perspective, we have established a rather non-intuitive notion that **pressure is**, in effect, **a flux of momentum**. Specifically, we discussed the *hydrostatic* pressure, i.e., that resulting from a transfer of the normal component of the momentum. (“Normal” means here the component that is parallel to the normal to the surface, i.e., perpendicular to the surface.) Hydrostatic pressure, by definition, corresponds to a force normal to the surface. The notion of pressure as a flux of momentum is quite different from the layman notion that pressure is some sort of restoring force from an environment, such as the restoring force your hand apparently feels when one squeezes

a spring or a well-inflated basketball. This layman notion of pressure as a restoring force from a squeezed spring is actually wrong. Though solids are quite different—and more complicated—than gases, the restoring force they exhibit upon deformation is of the same, kinetic origin that we have elucidated today. The only difference is that in solids or liquids, the atoms are confined by intermolecular forces, which, then, partially mitigate the effect of the atom's collisions with the outside environment.

Bonus discussion: Note that in addition to the flux of the normal component of the momentum, there is also often a flux of the *tangential* component of the momentum through a surface. Clearly, such transfer of the tangential momentum implies energy dissipation from the perspective of the incident particle, since the kinetic energy of the tangential motion of the incident particle will be decreased after the collision. (It is instructive to imagine that the particle “sticks” to the surface for a brief while and “drags” sideways.) This type of momentum transfer and the concurrent energy dissipation is responsible for the viscous drag. The quantity called *viscosity*, often denoted with the Greek letter η , quantitatively describes the efficiency of such momentum transfer. Accordingly, the aforementioned friction coefficient is proportional to the viscosity: $\zeta \propto \eta$, the proportionality coefficient depending on the object's shape. For instance, the friction coefficient for a sphere of radius R can be computed according to the Stokes formula: $\zeta = 6\pi R \eta$.

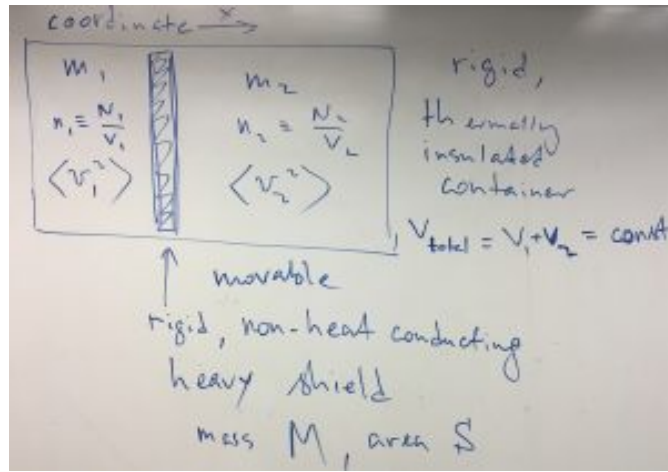
We have illustrated two types of transfer in this Chapter: particle transfer, via the particle flux $J \sim 1 \times (n v)$, and momentum transfer $p \sim (m v) \times (n v)$. These are two of the three major types of transfer phenomena, the remaining one being heat (or energy) transfer, to be discussed shortly.

Last but not least, the world as we know it is a story of bound states, as I stated in the beginning. We can now elaborate a bit more on this informal notion. Those bound states should be thought of the characters, or protagonists, in the story. The internal dynamics within each bound state are interesting and useful, as would be the feelings of an individual character in a story. Equally interesting and useful are the dynamics taking place when those bound states decay and new bound states form. These processes can be thought of as interactions between our “protagonists” and are accompanied by a transfer of matter, momentum, and energy. The corresponding fluxes, then, emerge as a statistics-centered way to describe the dynamics of the world. For instance, a chemical reaction should be properly thought of as a flux of a pertinent degree of freedom through the transition state. Likewise, transfer processes through a cell's membrane or absorption/desorption processes are all stochastic processes realized via particle fluxes.

4.

The temperature. Heat Transfer. Equilibrium. Equipartition of energy. The Ideal Gas Law

We begin this Chapter with a puzzler. Imagine the following setup, where a rigid, heat-insulated container is divided in two parts by a rigid piston that can freely move left or right. Each part contains a nearly ideal gas for which the following parameters are known: mass m , concentration $n = N/V$, and average velocity squared $\langle v^2 \rangle$. The quantities pertaining to the l.h.s. are labeled with “1”, and to the r.h.s. with “2”.



Clearly the ratio of the concentrations, n_1/n_2 is in one-to-one correspondence with the position of the piston and thus can be changed at will by moving the piston. Indeed, $n_1 = N_1/V_1$, $n_2 = N_2/V_2 = N_2/(V_{\text{total}} - V_1)$, where the total volume $V_{\text{total}} = V_1 + V_2$ remains constant by construction. Thus, $n_1/n_2 = (N_1/N_2)(V_{\text{total}} - V_1)/V_1$, where (N_1/N_2) is fixed, also by construction.

Now the puzzler: Suppose we prepare the system so that the following conditions are satisfied:

$$(1) \quad n_1 m_1 \langle v_1^2 \rangle = n_2 m_2 \langle v_2^2 \rangle$$

while

$$(2) \quad m_1 \langle v_1^2 \rangle \neq m_2 \langle v_2^2 \rangle$$

The puzzler is: Will the piston move or will it remain stationary? Is the system in true equilibrium or not?

We have seen in the preceding Chapter that the pressure

$$(3) \quad p = \frac{1}{3} m \langle v^2 \rangle n$$

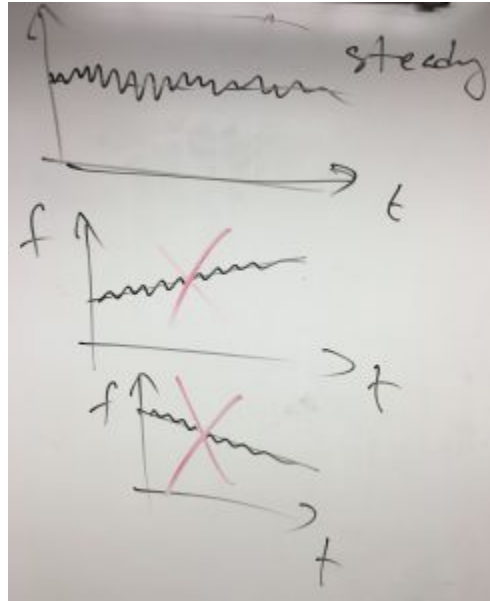
Suppose the area of the piston is S . Thus, the net force acting on the piston:

$$(4) \quad f = p_1 S - p_2 S = (p_1 - p_2) S$$

should vanish by Eqns. (1) and (3). Thus the piston is in a state of mechanical equilibrium and should stay put. Or, should it?

Before we proceed further, a short comment regarding the term “nearly ideal gas”. In a nearly ideal gas, the particles are almost never in contact with one another and collide (interact) just often enough to “thermalize”, or randomize their motions so that the particles sample all possible values of the velocity and coordinate without any

bias. As a result, any microscopic configuration will be visited again and again. This unbiased, recurrent sampling of a distribution that remains steady for an arbitrarily long time corresponds to a statistically steady, “equilibrated” system. In formal terms, equilibrium means that one may define a fixed, time-independent distribution for all the coordinates and velocities. Every quantity will fluctuate with in time, but the fluctuations each will be around a steady value:



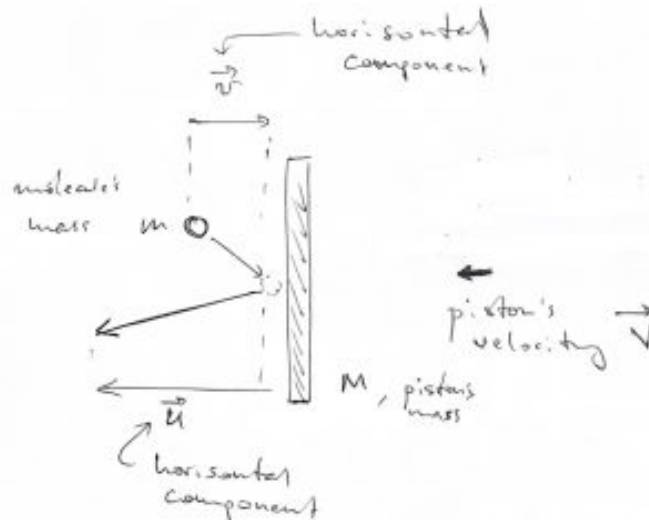
Only if this steady value remains steady *forever*, can we technically talk of “equilibrium”. In actuality, infinite observation times are unrealistic, and so when we say “infinite time”, we really mean “infinite, in principle”.

One useful property of a nearly ideal gas is that its energy is almost exclusively contained in the motion of the molecules, and almost none of it is stored in the potential energy:

$$(5) \quad E_{\text{kin}} \equiv \sum_i \frac{m_i v_i^2}{2} \gg V(\{\vec{r}_i\})$$

where by $\{\vec{r}_i\}$ we denote the full set of the coordinates of the particles.

Now back to our *puzzler*. As in the preceding Chapter, we are interested only in the horizontal component of particle’s velocity. The shield can move exclusively horizontally, by construction. Let us again use a formula we derived in Chapter 2 to write down an expression for the velocity u of particle that had just collided with a shield. The particle and the shield had velocities v and V , respectively, before the collision:



$$(6) \quad u = \frac{(m - M)v + 2MV}{m + M}$$

After we square this equation and average the resulting expression over the collisions—and, thus, over molecules—we obtain the following:

$$(7) \quad \langle u^2 \rangle = \frac{(m - M)^2 \langle v^2 \rangle + 4M^2 \langle V^2 \rangle + 4(m - M) \langle vV \rangle}{(m + M)^2}$$

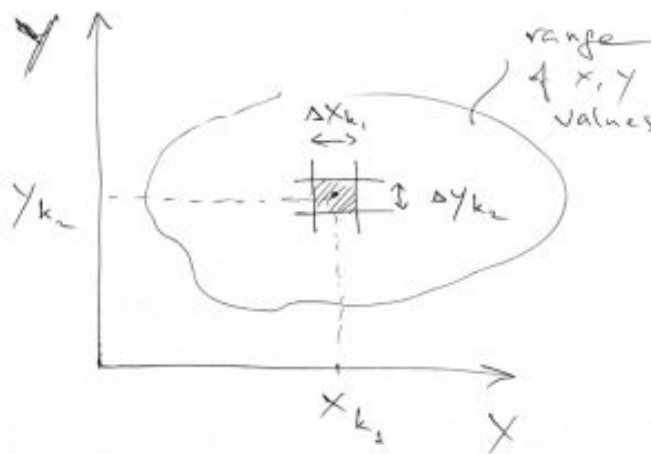
Let us see now that in the approximation where the velocity of an incoming particle and the velocity of the shield just prior to the collision are uncorrelated, the average of the product $\langle vV \rangle$ breaks up into the product of the respective averages of the two factors:

$$(8) \quad \langle vV \rangle = \langle v \rangle \langle V \rangle \text{ if } v \text{ and } V \text{ are uncorrelated}$$

Digression on statistics: Uncorrelated variables. Suppose we have two distributed quantities, call them x and y . Completely analogously to how we handled a single variable case in the last Chapter, one can compute the average of any combination of two variables using a weighted average. For concreteness, consider the product $x y$.

$$(9) \quad \langle x y \rangle = \sum_{k_1}^{M_1} \sum_{k_2}^{M_2} p_{k_1 k_2} x_{k_1} y_{k_2}$$

where we now sample two quantities, x and y . The quantity $p_{k_1 k_2}$ is the statistical weight (or probability) of a configuration where the variables x and y to *simultaneously* fall into a small rectangular sector $\Delta x_{k_1} \times \Delta y_{k_2}$ centered around the point (x_{k_1}, y_{k_2}) .



Because the variables x and y define a 2D space, these small rectangular sectors form a grid in that 2D space. Thus it is practical to use *two* indices to label those sectors. Other than this, the meaning of the weight $p_{k_1 k_2}$ is exactly the same as that of the weight p_k we defined for a single distributed quantity in the last Chapter.

Next, let us see that *the probabilities of uncorrelated events multiply*:

$$(10) \quad p_{k_1 k_2} = p_{k_1}^{(1)} p_{k_2}^{(2)}$$

where the weight p_{k_1} is the probability of outcome x_{k_1} in a standalone experiment involving the variable x and the weight p_{k_2} is the probability of outcome y_{k_2} in a standalone experiment involving variable y . The superscripts (1) and (2) are simply labels we need to distinguish the distribution functions for the two variables, which are generally different. We begin a simple example of two fair coins, each of which, if tossed, will land heads up or tails up with equal probability 1/2. Clearly there are four equally likely outcomes for an experiment where the two coins are tossed at the same time:

coin 1	coin 2	
heads	heads	
heads	tails	
tails	heads	
tails	tails	

Because there are 4 outcomes total and they are all equally likely, the probability of each outcome is exactly $1/4$. For instance, the probability to get two tails at the same time is $1/4$. On the other hand, the probability of getting tails for an individual fair coin is $1/2$. Consistent with Eq. (10), $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. By the same token, the probability to guess a 4-digit ATM code in one try is $\frac{1}{10,000}$ because there are 10,000 equally likely possibilities, i.e., numbers ranging from 0 to 9,999. Alternatively, one can look at this problem as the probability of guessing four uncorrelated one-digit numbers at the same time, again yielding $\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} \times \frac{1}{10} = \frac{1}{10,000}$.

These ideas are not difficult to generalize to arbitrary, “unfair” coins. Suppose you are tossing an unfair coin, call it “coin 1”, which yields heads with probability $p_1^{(1)} = 0.40$ (40%) and tails with probability $p_2^{(1)} = 0.60$ (60%). Suppose also that your friend is tossing, entirely independently of you, a different unfair coin, call it “coin 2”, whose outcomes are heads with probability $p_1^{(2)} = 0.70$ and tails with probability $p_2^{(2)} = 0.30$. Suppose you have tossed your coin a $N^{(1)} = 1000$ times. Let’s say your experiment yielded $N_1^{(1)} = 400$ heads. For each one of those heads, you know your friend had heads with probability $p_1^{(2)} = 0.70$, and so the number of outcomes that will count toward the “heads (coin 1) + heads (coin 2)” outcome, the top outcome entry in the Table above, is $N_1^{(1)} \times p_1^{(2)} = 400 \times 0.70 = 280$. Thus the statistical weight of the “heads-heads” outcome is $\frac{N_1^{(1)} \times p_1^{(2)}}{N^{(1)}} = \frac{N_1^{(1)}}{N^{(1)}} \times p_1^{(2)} = p_1^{(1)} \times p_1^{(2)} = 0.28$. Likewise, the probability of the “tails (coin 1) + heads (coin 2)” outcome is $p_2^{(1)} \times p_1^{(2)} = 0.12$ and so on. We see that the multiplication of probabilities comes about because the success rate of a compound event is conditional on the success of both of the constituent events. When the constituent events are statistically independent, the success rates of the individual events must be simply multiplied in order for us to determine the overall success rate. For this very reason, by the way, the rate of bimolecular reaction is proportional to the product of the activities (or concentrations) of the individual reactants: One needs one of *both* species to create a product molecule.

The converse of the above logic is of equal significance for this class: If it turns out that the compound statistical weight of events 1 and 2 is not determined by simply multiplying their individual statistical weights, we may say that there is a statistical *correlation*, or, in more physical terms, “interaction” between the two degrees of freedom, such as x and y in an above example. In practice, we may not know beforehand whether there is any interaction. This, then, raises a question: How do we determine the individual statistical weights, in the first place? Here is how to do this. Assuming that we have performed enough experiments to sample all relevant configurations of the system, we can histogram the chances of a specific outcome for the degree of freedom 1 where the degree of freedom 2 was not even monitored but, hopefully, has adequately sampled all of its configurations. The resulting histogram is, then, simply the sum of the combined statistical weight over all configurations of the degree of freedom 2:

$$(11) \quad p_{k_1}^{(1)} = \sum_{k_2} p_{k_1 k_2}$$

Likewise,

$$(12) \quad p_{k_2}^{(2)} = \sum_{k_1} p_{k_1 k_2}$$

Note that, by construction, $\sum_{k_1} p_{k_1}^{(1)} = 1$ and $\sum_{k_2} p_{k_2}^{(2)} = 1$. This automatically ensures that the combined distribution $p_{k_1 k_2}$ is normalized, too:

$$(13) \quad \sum_{k_1} \sum_{k_2} p_{k_1 k_2} = 1$$

This is particularly obvious when the two variables are statistically independent:

$$(14) \quad \sum_{k_1} \sum_{k_2} p_{k_1}^{(1)} p_{k_2}^{(2)} = \sum_{k_1} p_{k_1}^{(1)} \sum_{k_2} p_{k_2}^{(2)} = \sum_{k_1} p_{k_1}^{(1)} \times 1 = \sum_{k_1} p_{k_1}^{(1)} = 1$$

The above equations illustrate, among other things, how to manipulate double sums where the summed object is factorizable into a product, where one factor depends exclusively on one summation variable and the other factor depends exclusively on the other summation variable. By the same token, we can now compute the average of the product of two independent variables:

$$(15) \quad \begin{aligned} \langle x y \rangle &\equiv \sum_{k_1}^{M_1} \sum_{k_2}^{M_2} p_{k_1 k_2} x_{k_1} y_{k_2} = \sum_{k_1}^{M_1} \sum_{k_2}^{M_2} p_{k_1}^{(1)} p_{k_2}^{(2)} x_{k_1} y_{k_2} \\ &= \sum_{k_1}^{M_1} p_{k_1}^{(1)} x_{k_1} \sum_{k_2}^{M_2} p_{k_2}^{(2)} y_{k_2} = \sum_{k_1}^{M_1} p_{k_1}^{(1)} x_{k_1} \langle y \rangle = \langle y \rangle \sum_{k_1}^{M_1} p_{k_1}^{(1)} x_{k_1} \\ &= \langle y \rangle \langle x \rangle = \langle x \rangle \langle y \rangle \end{aligned}$$

If you do not feel comfortable with this type of algebraic manipulations, it may be worthwhile to practice by writing out such double sums explicitly for small values of M_1 and M_2 .

Now, we can show, using the same logic as above, that the compound probability of three or more uncorrelated events also multiply. Indeed, one can relabel the compound experiment concerning, say, coin 2 and coin 3 as experiment 2 and repeat the argument. To summarize, for an arbitrary number of distributed variables, N :

(16)

$$\begin{aligned} p_{k_1 k_2 \dots k_N} &= p_{k_1}^{(1)} p_{k_2}^{(2)} \times \dots \times p_{k_N}^{(N)} \quad \text{variables uncorrelated, statistically independent} \\ p_{k_1 k_2 \dots k_N} &\neq p_{k_1}^{(1)} p_{k_2}^{(2)} \times \dots \times p_{k_N}^{(N)} \quad \text{variables correlated, interactions present} \end{aligned}$$

End of statistics digression.

Now that we have established the (approximate) validity of Eq. (8), we are ready to formulate conditions for true equilibrium. Indeed, in true equilibrium, the piston is not moving, on average: $\langle V \rangle = 0$, which implies, by Eq. (8), that

$$(17) \quad \langle vV \rangle = 0$$

Furthermore, in equilibrium, all directions in space must be equivalent or, else, there would be a net flow of particles or other properties. For example, suppose for a moment that two opposite directions are not equivalent in that the particle flux in one direction is not equal to the particle flux in the opposite direction. In that case, there would be a non-vanishing *net* flow along this direction which would, then, result in a continuing piling up of particles in one place and a continuing “drain” of particles in another place. In addition, the concentration should be on average spatially uniform, too, so as to also prevent a net flow. Because the flux is the product of the concentration and velocity, respectively, the velocities of individual particles should be distributed in a way that is independent of the place and direction. For this reason, we must conclude that the characteristics of the incoming and outgoing particles, near the “collision zone”, should be on average the same:

$$(18) \quad \langle u^2 \rangle = \langle v^2 \rangle$$

Eqs. (7), (17), and (18) then yield, after a bit of algebra, a remarkably consequential result:

$$(19) \quad \frac{m\langle v_x^2 \rangle}{2} = \frac{M\langle V_x^2 \rangle}{2}$$

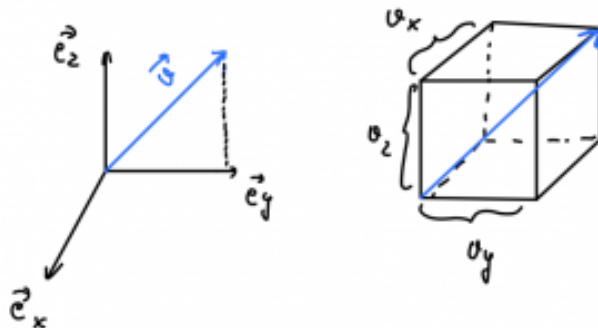
where I have added the $1/2$ factors for future convenience and the subscript x to emphasize that we are dealing with motion along the coordinate axis x . What Eq. (19) tells us that the kinetic energy of the motion of each particle and the piston must be mutually equal in equilibrium, on the average! Since this applies to the molecules on *both* sides of the piston, we conclude that in equilibrium,

$$(20) \quad \frac{m_1\langle v_{x,1}^2 \rangle}{2} = \frac{m_2\langle v_{x,2}^2 \rangle}{2}$$

Let us refocus on an individual compartment of our original setup. Since the directions x , y , and z are all equivalent in equilibrium, one has it that

$$(21) \quad \frac{m\langle v_x^2 \rangle}{2} = \frac{m\langle v_y^2 \rangle}{2} = \frac{m\langle v_z^2 \rangle}{2}$$

At the same time, the velocity vector can be decomposed into three mutually orthogonal components:

$$\vec{v} = v_x \vec{e}_x + v_y \vec{e}_y + v_z \vec{e}_z$$


Thus

$$(22) \quad v^2 = v_x^2 + v_y^2 + v_z^2$$

By the way, because of this geometrical relation, the kinetic energy of motion in spatial dimensions greater than 1 is simply the sum of the kinetic energies of motion along individual directions:

$$(23) \quad \frac{m\langle v^2 \rangle}{2} = \frac{m\langle v_x^2 \rangle}{2} + \frac{m\langle v_y^2 \rangle}{2} + \frac{m\langle v_z^2 \rangle}{2}$$

In any event, Eq. (22) yields

$$(24) \quad \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

Which, then, leads, by Eq. (21), to :

$$(25) \quad \frac{m\langle v_x^2 \rangle}{2} = \frac{m\langle v_y^2 \rangle}{2} = \frac{m\langle v_z^2 \rangle}{2} = \frac{1}{3} \frac{m\langle v^2 \rangle}{2}$$

In view of Eq. (20), this yields that in equilibrium, the average kinetic energy of a molecule on the l.h.s and a molecule on the r.h.s., respectively, must be the same:

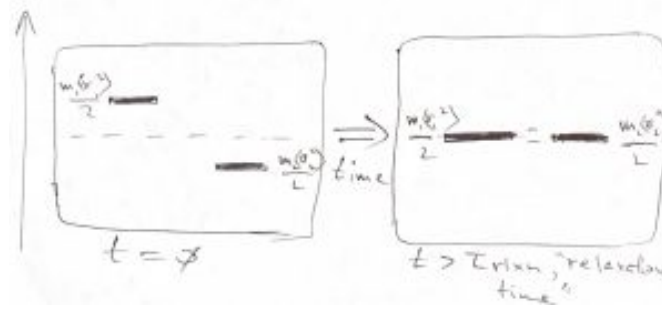
$$(26) \quad \frac{m_1\langle v_1^2 \rangle}{2} = \frac{m_2\langle v_2^2 \rangle}{2}$$

On the basis of Eq. (20) or (26) we then find the answer to the puzzler: The piston will actually move because the assumption of the piston being stationary is inconsistent with the condition (2). What gives?? After all, the piston appears to be in mechanical equilibrium, by Eq. (1)! The answer is that condition (1) only ensures that

the net mechanical force on the piston vanishes only on the average, but not necessarily at any given moment. This uncompensated force, which fluctuates around zero, then leads to fluctuations in the position of the piston and a gradual drift either leftward or rightward, the direction depending on the sign of inequality in Eq. (2), to be determined shortly. Suppose, for concreteness, that in the beginning:

$$(27) \quad \frac{m_1 \langle v_1^2 \rangle}{2} > \frac{m_2 \langle v_2^2 \rangle}{2} \quad t = 0$$

To actually reach equilibrium, the piston should be moving in the direction such that the quantity $\frac{m_1 \langle v_1^2 \rangle}{2}$ should be decreasing over time, while the quantity $\frac{m_2 \langle v_2^2 \rangle}{2}$ should be increasing over time so as to meet somewhere midway by the time equilibrium is reached:



To understand what is happening physically, we note that the total kinetic energy of the gas on the l.h.s., $E_1 = N_1 \frac{m_1 \langle v_1^2 \rangle}{2}$ is decreasing, while the total kinetic energy of the gas on the r.h.s., $E_2 = N_2 \frac{m_2 \langle v_2^2 \rangle}{2}$ is decreasing as the system is approaching equilibrium. In other words, the energy stored in the motions of the particles is being transferred, while no other property is being transferred at the same time. Indeed, the pressures in the two compartments are mutually equal (no momentum transfer) and there is no particle transfer either (the piston is impermeable by construction).

What do we make out of this type of energy transfer, where just the kinetic energy of the molecules' motion is moved from one place to another, while no macroscopically observable quantity is transferred and there are no visible changes in the shape or position of the objects involved? This is the familiar **heat transfer**! The above argument also provides a simple criterion for the direction of heat transfer, if any: Heat will flow from places where the quantity $\langle mv^2/2 \rangle$ is greater to places where the quantity $\langle mv^2/2 \rangle$ is lower. This means the quantity $\langle mv^2/2 \rangle$ is a good proxy for what we call the **temperature**. In fact, by convention, we define temperature T so that:

$$(28) \quad k_B T \equiv \frac{1}{3} \langle mv^2 \rangle$$

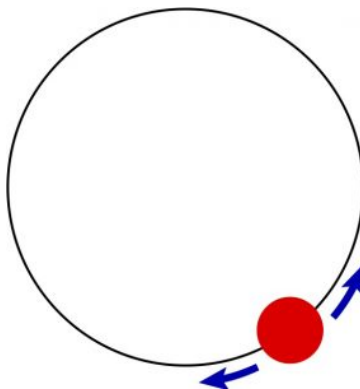
We have included the mass of the molecule inside the average to account for the possibility that more than one species can be present in the system. Recall that Eq. (26) was written with two pure gases separated by a partition, but applies equally well to a *mixture* of two nearly ideal gases. In any event, the above definition of the temperature is clearly not unique. Any other definition where T is a monotonically increasing function of $\langle mv^2 \rangle/2$ would be workable, but the linear dependence in the above definition happens to be quite convenient, as we will have a chance to witness many times in the future.

The Boltzmann constant $k_B = 1.38 \cdot 10^{-23} \text{ J/K}$, is just that: a numerical constant used to convert from temperature to energy. Really, temperature has the meaning of energy, consistent with its definition of being equal, up to a multiplicative constant, to the kinetic energy of molecules.

The numerical factor of $1/3$ in Eq. (28) is quite arbitrary as well, but it is the convention that must be followed consistently. With this convention, we obtain that the average kinetic energy of motion per single degree of freedom is exactly $k_B T/2$:

$$(29) \quad \frac{\langle mv_x^2 \rangle}{2} = \frac{\langle mv_y^2 \rangle}{2} = \frac{\langle mv_z^2 \rangle}{2} = \frac{1}{3} \frac{\langle mv^2 \rangle}{2} = \frac{k_B T}{2}$$

a fact often referred to as the **Equipartition Theorem**. A “degree of freedom” is something whose configuration can be described by a single number. For, instance, motion in 3D space corresponds with three degrees of freedom. We can extend these notions to motions other than purely translational motions. For instance, a rotation around a fixed axis corresponds with a single degree of freedom. Indeed, one can think of such a rotation as a translation of a bead confined to moving in a circle:



And so, for each rotation, there is a $k_B T/2$ worth of energy. Another classic example is a harmonic oscillator. This system has also a potential energy. We have seen, however, that on the average, the kinetic and potential energy of the harmonic oscillator are equal. Thus the total energy of a harmonic oscillator, on average is just the $k_B T$. Non-withstanding the fact that these statements must be sometimes corrected for quantum-mechanical effects (and will be in due time), it is an incredibly useful notion that the typical thermal energy of a single degree of freedom is typically around $k_B T$.

Next we combine Eq. (28) with the earlier derived relation for pressure: $p = \frac{1}{3} n m \langle v^2 \rangle$ to obtain the **Ideal Gas Law**:

$$(30) \quad p = n k_B T$$

Note all the quantities in the above equation are *intensive*, i.e., provide no information about the size of the system. The concentration n can be easily rewritten in terms of *extensive* variables, which, by definition, scale linearly with the system size. Indeed, $n = N/V$, which, then, yields

$$(31) \quad p = \frac{N}{V} k_B T$$

or

$$(32) \quad p V = N k_B T$$

Alternative ways to write down the Ideal Gas Law is

$$(33) \quad p V = \frac{N}{N_A} N_A k_B T$$

$$\Rightarrow p V = \nu R T$$

where $\nu \equiv N/N_A$ is the number of moles and $R \equiv k_B \cdot N_A = 8.31 \text{ J/(mol K)}$ is the universal gas constant. Also common, but unphysical way to write the ideal gas law is in terms of the molar volume $V_m \equiv V/\nu$:

$$p V_m = R T$$

The Ideal Gas Law is both a definition of the temperature and a physical law. How does this work? We can use, as our “thermometer”, a specific gaseous substance that we think behaves like a nearly ideal gas and then make predictions about *other* gases. For instance, the ideal gas law allows one to predict the temperature of a gas, if its concentration and pressure are known. One, then, can compare this prediction by bringing test “test gas”

in mechanical and thermal contact with our “thermometer gas” prepared at the same pressure and see, whether heat exchange will take place. In practice, we use thermometers that work using other physical phenomena. Nearly ideal gases are used to calibrate those more practical thermometers in a temperature range where we expect a gas behave nearly ideally. Making sure that temperature measurements are properly standardized in a broad temperature range requires much sophistication, engineering skill, and knowledge of Thermodynamics and Statistical and Quantum Mechanics.

We finish by returning to our puzzler. Suppose that the system was prepared so that $\frac{m_1 \langle v_1^2 \rangle}{2} > \frac{m_2 \langle v_2^2 \rangle}{2}$, which we now know corresponds with $T_1 > T_2$. Recall that the pressures remain fixed and mutually equal all along, as the mechanical equilibrium is never compromised: $p_1 = p_2 = \text{const}$. Now, as the *full* equilibrium is approached and the two temperatures converge onto some value midway, the concentration of gas 1 must increase while the concentration of gas 2 must decrease with time, by the ideal gas law: $p_1 = p_2 \Rightarrow \frac{n_1}{n_2} = \frac{T_2}{T_1}$. This means that the piston will be moving to the *left* until equilibrium is achieved. Makes sense, doesn't it?

Final remark: We assumed above that the piston is truly rigid to drive home the point that if one neglected thermal fluctuations, one would miss a very important aspect of equilibration in the form of heat exchange. In reality, a piston would have to be made out of molecules, too, and so it would conduct heat much more efficiently than the idealized piston we had in mind. Depending on how well the piston conducts heat, the temperatures in the respective compartments may not be actually uniform. These minor complications are not show stoppers and would distract us from the meat of the argument. Also, we did not mention that the piston's coordinate and velocity would be fluctuating not just in one, but in all spatial directions, again because of the equipartition.

5.

The Gibbs-Boltzmann distribution. The Maxwell distribution of velocities.

In the preceding Chapter, we connected a dynamical description of matter at the molecular level with macroscopic observables, such as pressure and temperature, no small feat. Furthermore, we were able to make predictions about the time evolution of the system. To make the connection, we applied notions of statistics. We have assumed that there is a steady state ensemble of configurations (or “microstates”) the system will continue to revisit at a steady rate, on the average, and in no particular order. (The rate may be extremely small, but it should be non-vanishing. If a microstate has been visited once, it should be visited again and again in perpetuity.) The assumption of such recurrent sampling of all available configurations in random order—sometimes referred to as the “ergodic hypothesis”—is not innocent; its validity must be decided on a case to case basis. When the assumption does hold, one can say that the system can achieve equilibrium. Equilibrium is something that may take some time to establish after the system was prepared since there is no guarantee that the system was prepared in a typical configuration. This is analogous to the so called “beginners’ luck” in gambling, which typically runs out as the gambler continues to play. With these provisos in mind, let us now extend our treatment from nearly non-interacting gases to systems where particles actually interact; in the vast majority of systems of practical interest, interactions are present and are significant. We will continue to assume that equilibrium can be, in fact, established.

First off, what is “interaction”? In dynamical terms, interaction between two objects means that one object imposes some constraints on the motion of the other object. Consider the following energy function for two degrees of freedom:

$$\begin{aligned} E &= \frac{m_1 v_1^2}{2} + V_1(x_1) \\ &+ \frac{m_2 v_2^2}{2} + V_2(x_2) \\ (1) \quad &+ V_{\text{int}}(x_1, x_2) \end{aligned}$$

where $v_1 = dx_1/dt$ and $v_2 = dx_2/dt$ are the velocities corresponding to the degrees of freedom 1 and 2, respectively.

The top line on the r.h.s. contains terms that depend exclusively on the coordinate and velocity of particle 1. The middle line contains terms that depend exclusively on the coordinate and velocity of particle 2. In contrast, the bottom line contains a function that depends on the configuration of *both* particles. The full potential energy is, then, a sum of three terms:

$$(2) \quad V(x_1, x_2) = V_1(x_1) + V_2(x_2) + V_{\text{int}}(x_1, x_2)$$

By construction, the term $V_{\text{int}}(x_1, x_2)$ can not be decomposed into a sum of some function that depends solely on x_1 and some function that depends solely on x_2 :

$$(3) \quad V_{\text{int}}(x_1, x_2) \neq U(x_1) + U(x_2)$$

Clearly, then, the force acting on object 1 is modified by the presence of object 2, because differentiation with respect to x_1 does not rid us from the variable x_2 in the expression for the force acting on particle 1:

$$(4) \quad f_1 = -\frac{\partial V(x_1, x_2)}{\partial x_1} = -\frac{dV(x_1)}{dx_1} - \frac{\partial V_{\text{int}}(x_1, x_2)}{\partial x_1}$$

which is clearly a function of both x_1 and x_2 . Indeed, suppose, to the contrary, that $\frac{\partial V_{\text{int}}(x_1, x_2)}{\partial x_1}$ is not a function of x_2 , thus implying $\frac{\partial V_{\text{int}}(x_1, x_2)}{\partial x_1} = C_1(x_1)$, where $C_1(x_1)$ is some function of x_1 but not x_2 . Integrating this equation with respect to x_1 yields $V_{\text{int}}(x_1, x_2) = \int^{x_1} C_1(x) dx + C_2$, where C_2 is x_1 independent. (C_2 could be a function of x_2 .) But this kind of additive form is expressly forbidden by the condition (3), thus proving that for non-additive potentials, object 2 exerts a force on object 1. By the same token, the force acting upon object 2 will depend on x_1 as well. The presence of a term $V_{\text{int}}(x_1, x_2)$ of the kind satisfying condition (3), in the full energy function, thus means the degrees of freedom in question are interacting, or “coupled”.

More generally, we can state that a set of degrees of freedom are non-interacting, if the full energy function is additive, i.e., it can be decomposed into a sum of energy functions each pertaining to an individual degree of freedom and there are no “cross-terms” that couple the degrees of freedom:

$$(5) \quad E = \sum_i E^{(i)} \Rightarrow \text{no interaction}$$

where $E^{(i)} \equiv E^{(i)}(x_i, v_i)$ is the energy function for the degree of freedom i .

The above notions on the additivity of energies of independent degrees of freedom have two very important implications:

1. Energy can be used as an indicator for whether interactions have actually occurred. Indeed, we saw that interactions change the state of the motion of the system—sometimes referred to as the “microstate”—since they amount to a non-vanishing force, by Eq. (4). Thus changes in the value of the energy can be used to bookkeep the microstates of a system. Indeed, two distinct values of energy necessarily correspond to two distinct microstates. The converse is not necessarily true, however. Furthermore, a great deal of ambiguity arises when two or more distinct microstates are degenerate, i.e. have the same value of energy. This ambiguity is thus intrinsically built into a bookkeeping scheme based on energies and, as we will see later, is impossible to avoid in practice. Fortunately, this complication can (and will) be dealt with and has colossal significance in applications.
2. The lack of mutual correlation between two degrees of freedom, whose energies simply add to make up the total energy, allows one to explicitly determine the functional form of the dependence of the probability p_i of microstate i on the energy E_i of that microstate. This is because probabilities of independent events multiply, as we saw earlier.

Let’s work this out mathematically. Since we have agreed that the energy is the only quantity we will keep track of, the probability of microstate i is determined exclusively by its energy E_i :

$$(6) \quad p_i = \frac{g(E_i)}{Z}$$

where g is a specific but unknown, as of yet, function, and the quantity

$$(7) \quad Z \equiv \sum_i g(E_i)$$

is a normalization factor ensuring our probabilities are normalized:

$$(8) \quad \sum_i p_i = \frac{1}{Z} \sum_i g(E_i) = \frac{1}{Z} Z = 1$$

which formally reflects the notion that the system is in *some* microstate with probability one. As written in

Eq. (6), the definition of the function $g(E_i)$ is still ambiguous. Indeed, if we multiplied all of the $g(E_i)$'s by a fixed number, the value of the weights p_k would not change since Z would *also* be multiplied by the same fixed number, by Eq. (7). To remove this ambiguity, we impose an additional condition that the quantity Z be equal to the total number of *accessible* microstates, subject to some constraints of choice. (Common constraints include things like fixing the temperature and/or volume of the system, or maintaining a certain value of pressure and particle number, etc.) The number of accessible states has a spooky property that it does not have to be integer, in seeming conflict with the expectation that the number of configurations can be obtained by ordering them in some way and then counting them using ordinal numbers. I will illustrate how this apparent lack of ordinality comes about using an example. Suppose you live in a 3-story home and your friend lives in a 5-story home; each story has exactly one room. Clearly you can be in one room at a time, and so there are 3 distinct configurations when you are home. Likewise, your friend has 5 distinct configurations, and the compound you+friend system has $3 \times 5 = 15$ distinct configurations. Indeed, for each of your 3 configurations, your friend has 5. Now suppose you really don't like going upstairs much because your wi-fi router is on the ground floor and the signal quality deteriorates as you go upstairs. (This is your constraint.) As a result, you spend say, 60% of your time on floor 1, 30% on floor 2, and the remaining 10% on floor 3. Being the likeliest one, the 1st floor configuration is counted as unconditionally accessible and so contributes exactly 1 to the total number of accessible configurations. The 2nd floor configuration contributes only $\frac{30\%}{60\%} = \frac{1}{2}$, and the 3rd floor configuration contributes only $\frac{10\%}{60\%} = \frac{1}{6}$. The resulting accessible number of configurations is, then, $Z_1 = 1 + \frac{1}{2} + \frac{1}{6} = 1\frac{7}{12} \approx 1.583$. It is substantially less than the number of configurations that would be accessible without any constraints, i.e., 3. This type of reasoning may strike you as odd, so let's look at a simpler yet more extreme example. Suppose you have a fair coin. Clearly there are exactly two distinct configurations: heads and tail. Correct? Now suppose the coin is slightly unfair, say, the odds of heads vs. tails are 5 vs. 4. How many accessible configurations does that correspond to? To drive home the point that this number is less than 2, imagine instead that the odds are grotesquely skewed toward heads, say, $e^{10^{23}}$ vs. 1. Nobody in their right mind would bet even a penny on the possibility of observing tails, since $1/e^{10^{23}}$ is equivalent to zero for all intents and purposes. This means that the accessible number of states for this grossly unfair coin is just one, the accessible state being the heads. The number of accessible states for the slightly unfair coin, in a sense, interpolates between the fair coin and the grossly unfair coin, yielding: $1 + \frac{4}{5} = 1.8$. Now suppose your friend has a similar problem with her wi-fi in *her* house and her odds of being on floors 1 through 5 are, respectively: 40%, 30%, 20%, 7%, and 3%. The resulting number of accessible states is, then $Z_2 = 1 + \frac{30}{40} + \frac{20}{40} + \frac{7}{40} + \frac{3}{40} = 2.5 < 5$. And what is the total number of accessible states for the compound you+friend system? It is $Z_1 \times Z_2 = 1\frac{7}{12} \times 2\frac{1}{2} \approx 3.96$, well below the 15 states that would be accessible without the constraints.

Now consider a general compound system consisting of two non-interacting subsystems, 1 and 2, and label their microstates with indices k_1 and k_2 , respectively. The probability of microstate k_1 , whose energy is $E_{k_1}^{(1)}$, is, then

$$(9) \quad p_{k_1}^{(1)} = \frac{1}{Z^{(1)}} g(E_{k_1}^{(1)})$$

Likewise, the probability of microstate k_2 , whose energy is $E_{k_2}^{(2)}$ for system 2 is

$$(10) \quad p_{k_2}^{(2)} = \frac{1}{Z^{(2)}} g(E_{k_2}^{(2)})$$

$Z^{(1)}$ is the number of accessible states for system 1 and $Z^{(2)}$ for system 2.

On the one hand, the probability to observe states k_1 and k_2 simultaneously is given by the product of the probabilities of the standalone probabilities, as we discussed in the preceding Chapter:

$$(11) \quad p_{k_1 k_2} = p_{k_1}^{(1)} p_{k_2}^{(2)}$$

On the other hand, Eq. (6) tells us the probability of the (k_1, k_2) configuration is

$$(12) \quad p_{k_1 k_2} = \frac{1}{Z} g(E_{k_1}^{(1)} + E_{k_2}^{(2)})$$

because the energy of the combined system is simply $E_{k_1}^{(1)} + E_{k_2}^{(2)}$. Furthermore, the total number of accessible states is determined by multiplying those numbers for the standalone systems 1 and 2, as we discussed above:

$$(13) \quad Z = Z^{(1)} Z^{(2)}$$

Putting together Eqs. (28)-(13) yields

$$(14) \quad g(E_{k_1}^{(1)} + E_{k_2}^{(2)}) = g(E_{k_1}^{(1)}) \times g(E_{k_2}^{(2)})$$

This equation applies for any values of the two quantities $E_{k_1}^{(1)}$ and $E_{k_2}^{(2)}$ and, thus, defines a functional equation for the (yet unknown) function $g(x)$:

$$(15) \quad g(x + y) = g(x) g(y), \text{ for any two arguments } x \text{ and } y$$

Functional equations generally do not have a unique solution and are often hard to solve. But, in this particular case, we are in luck since the solution is not hard to find and is sufficiently unique for our purposes. First, set $y = 0$ in Eq. (15) to convince yourself that

$$(16) \quad g(0) = 1$$

Next, differentiate Eq. (15) with respect to y , where one must use the chain rule for the l.h.s.: $\frac{\partial g(x+y)}{\partial y} = g'(x+y) \frac{\partial(x+y)}{\partial y} = g'(x+y) \times 1 = g'(x+y)$, where the prime means the derivative with respect to the argument of the function:

$$(17) \quad f'(x) \equiv \frac{df}{dx}$$

And so one gets

$$(18) \quad g'(x + y) = g(x) g'(y)$$

Now again set $y = 0$ to obtain

$$(19) \quad g'(x) = -\beta g(x)$$

where defined the constant β to equal the negative derivative of g at the origin:

$$(20) \quad \beta \equiv -g'(0) \equiv -dg/dx|_{x=0}$$

The minus sign is artificial but will make life easier in the future. Eq. (19) is easily solved by separating the variables and integrating: $dg/g = -\beta dx \Rightarrow \ln g = -\beta x + \text{const}$, where the constant is fixed at $\text{const} = 0$, in view of Eq. (16). As a result, we obtain a remarkably simple expression for the function g :

$$(21) \quad g(E) = e^{-\beta E}$$

We are left with determining the coefficient β . Consider a particle freely moving in 1D (“moving freely” = “not subjected to an external force”): $E = \frac{mv_x^2}{2}$, where I used the subscript x to emphasize that the motion is along one spatial direction, chosen to be x for concreteness. Distinct microstates of the particles differ only by their velocities and, in fact, are uniquely labelled by the corresponding value of v_x itself. Hence,

$$(22) \quad p(v_x) \propto C e^{-\beta m v_x^2 / 2}$$

where the v -independent proportionality constant can be determined by requiring that the distribution be normalized to 1: $\int_{-\infty}^{\infty} p(v_x) dv_x = 1$. This yields, after consulting the table of definite integrals: $\int_{-\infty}^{\infty} e^{-\alpha y^2} dy = (\pi/\alpha)^{1/2}$:

$$(23) \quad p(v_x) = \left(\frac{\beta m}{2\pi} \right)^{1/2} e^{-\frac{\beta m v_x^2}{2}}$$

Next we compute the average of the velocity squared:

$$(24) \quad \langle v_x^2 \rangle \equiv \int_{-\infty}^{\infty} v_x^2 p(v_x) dv_x = \frac{1}{\beta m}$$

On the other hand, in the preceding Chapter we defined the temperature according to $k_B T = m \langle v_x^2 \rangle$. This immediately yields:

$$(25) \quad \beta = \frac{1}{k_B T}$$

As a result we may write, for the probability of state k , what is called the *Gibbs-Boltzmann distribution*:

$$(26) \quad p_i = \frac{e^{-\beta E_i}}{Z}$$

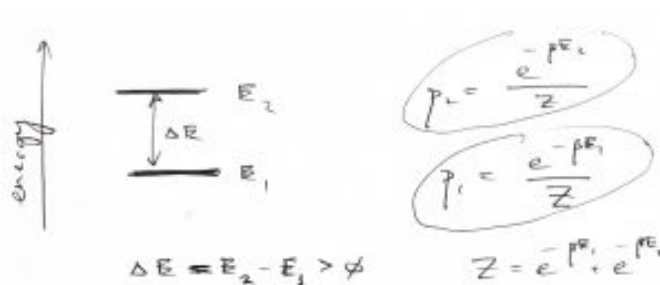
where the number of accessible states:

$$(27) \quad Z \equiv \sum_i e^{-\beta E_i}$$

is sometimes called the *partition function*, because it shows how the overall number of accessible states is partitioned among distinct microstates.

Eq. (26), together with Eqs. (25) and (27) of course, is arguably the most important result of Thermodynamics and Statistical Mechanics! The velocity distribution in Eq. (23) is *also* quite important in its own right. It is called the *Maxwell distribution* of velocities.

It is worthwhile to consider the simplest non-trivial arrangement where there are two exactly two states. Such a two-level system is a good model for the electronic or nuclear spin 1/2 in a magnetic field. The two microstates correspond to the spin up and down. The lowest energy state is called the ground state. States at higher energies are called excited states. There is only one excited state in a two-level system, of course.



According to Eq. (6) and (7),

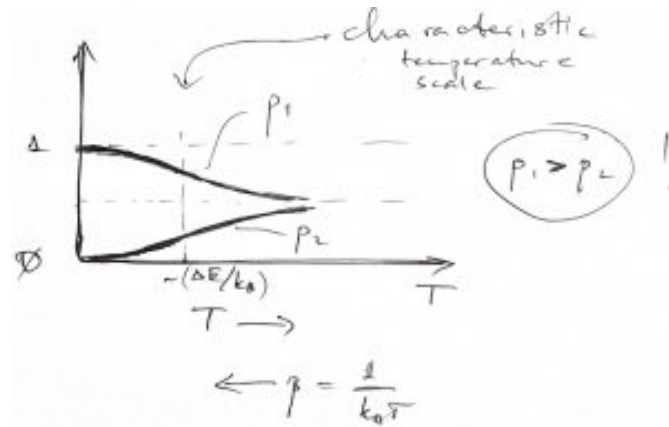
$$(28) \quad p_1 = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2}} = \frac{1}{1 + e^{-\beta \Delta E}}$$

and

$$(29) \quad p_2 = \frac{e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}}$$

Note $p_2 = 1 - p_1$, as it should, and that the probabilities depend only on energy differences, *not* the absolute values of energies. This is consistent with our earlier realization that only increments of the potential energy matter, not its absolute value. In other words, observable quantities should be independent of the energy reference. (Note forces are observable, energy is not!)

We next sketch the two weights p_1 and p_2 .



We note that $p_1 > p_2$ always, i.e., the ground state of the two-level system is always likelier to be occupied than the excited state. Only in the limit of infinite temperature, $T \rightarrow \infty$, $\beta \rightarrow 0$, do the two states become equally likely. Incidentally, this is the limit where the number of accessible states, Z , approaches its largest possible value of 2.

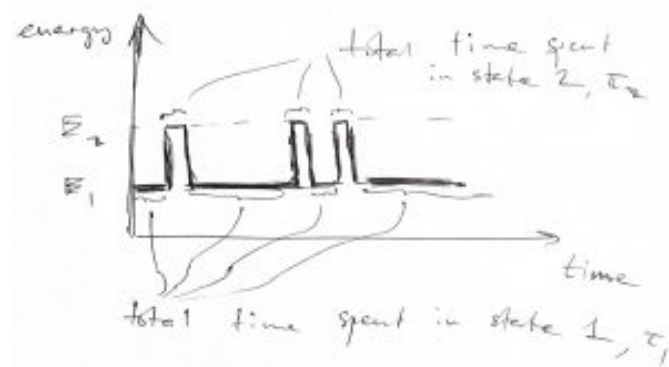
Let's review the meaning of the word “probability” in a practical context. One way to connect the weights p_k to experiment is that given a (large) number N of identical systems, we expect that at any given time: $N_1 = p_1 N$ will be in state 1, while $N_2 = p_2 N$ will be in state 2. Hereby,

$$(30) \quad p_1 = \frac{N_1}{N_1 + N_2}$$

$$(31) \quad p_2 = \frac{N_2}{N_1 + N_2} = 1 - p_1$$

, consistent with Eqs. (28) and (29). This is an example of *ensemble averaging*. Here you are looking at *many equivalent systems at the same time*.

Alternatively, one can determine the odds for a two-level system to be in state 1 or 2 by bookkeeping the amount time just one such system spent in those states. Here you monitor *one system over a long time*, this is called *time averaging*:



$$p_1 = \frac{\tau_1}{\tau_1 + \tau_2}$$

$$p_2 = \frac{\tau_2}{\tau_1 + \tau_2} = 1 - p_1$$

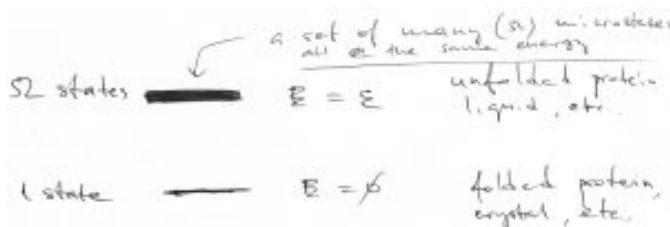
c.f. Eqs. (30) and (31).

Various quantities of interest can be determined using the statistical weights p_i . For instance, the expectation (or average, or mean) value of the energy is

$$\langle E \rangle = \sum_i p_i E_i = E_1 p_1 + E_2 p_2 \quad (32)$$

Note the expectation value of energy is never equal to its instantaneous value—i.e. the energy of either microstate—but, instead, interpolates between E_1 and E_2 . Note also that because $p_2 < p_1$, the largest energy the system can have is $\frac{E_1 + E_2}{2}$.

The only way to raise the expectation value of the energy is to employ more excited states. Consider, then, a more complicated example, where there is still just one ground state, at energy $E = 0$, but there are Ω excited states, each at energy $E = \varepsilon$. The quantity Ω is often referred to as the degeneracy of the excited state. One must be careful and remembering that there are actually Ω *distinct* excited states.



As before, the probability to be in a particular state is determined by the Boltzmann-Gibbs distribution

$$p_i = \frac{e^{-\beta E_i}}{Z} \quad (33)$$

while the partition function Z is given by

$$Z = \sum_i e^{-\beta E_i} = 1 + \Omega e^{-\beta \varepsilon} \quad (34)$$

We number the states starting from the ground state and use that $E_1 = 0$ and $E_i = \varepsilon$ for $i > 1$, by construction.

The expectation value of the energy is now:

$$\langle E \rangle = \sum_i p_i E_i = \frac{1}{1 + \Omega e^{-\beta \varepsilon}} 0 + \frac{\Omega e^{-\beta \varepsilon}}{1 + \Omega e^{-\beta \varepsilon}} \varepsilon \quad (35)$$

where we wrote out explicitly the ground and excited state energies 0 and ε to drive home that the question of the probability to have a certain amount of energy is generally very different from the question of the probability to be in a microstate with that energy.

Indeed, the probability to have energy $E = \varepsilon$ is

$$p(E = \varepsilon) = \sum_{i: E_i = \varepsilon} p_i = \frac{\Omega e^{-\beta \varepsilon}}{1 + \Omega e^{-\beta \varepsilon}} \quad (36)$$

and can be made as close to one as we want by making the degeneracy Ω larger.

It may be simple, but this model is not a bad approximation for the energy landscape of a protein molecule. Here the ground, lowest energy state would correspond to the protein molecule folded in its native state. Each of the unfolded states is significantly higher in energy than the native state and, individually, have no chance against the native state. When considered together, however, the unfolded states can take over given a high enough temperature. Indeed the probability to be unfolded relative to being folded is given by ratio:

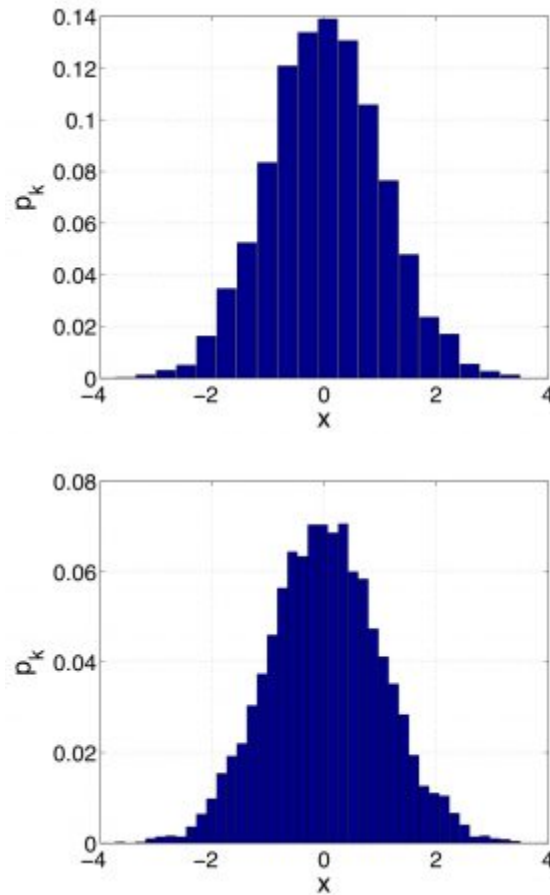
$$(37) \quad \frac{p(E = \varepsilon)}{p(E = 0)} = \Omega e^{-\beta \varepsilon}$$

At the special value of temperature, called the folding temperature T_f , this ratio is equal to one implying the protein molecule is equally likely to folded or unfolded. Thus,

$$(38) \quad k_B T_f = \frac{\varepsilon}{\ln \Omega}$$

Can you see that at $T > T_f$, the $\frac{p(E=\varepsilon)}{p(E=0)}$ is greater than one, implying the protein molecule is likely unfolded? And vice versa for $T < T_f$. Your homework problems highlight just how readily the equilibrium is shifted toward the folded state or the unfolded states as the temperature is moved away from T_f . In any event, increasing the multiplicity of the unfolded states clearly decreases the folding temperature. This makes sense, doesn't it?

It is now time for another **Digression on Statistics**: We saw just moments ago that in some cases, a variable that one can use to label distinct microstates is a truly continuous variable, such as the velocity in Eq. (23). This does not prevent one from histogramming this variable, of course, but it may now be practical to use a histogram where the width of the bar is arbitrarily narrow. One reason to do this is that if in the limit of a vanishingly narrow histogram bin, the histogram becomes smooth and, hence, becomes amenable to a variety of mathematical operations, such as differentiation. Integration becomes much easier, too. One problem with shrinking the bin size is that the number of data points decreases, too, roughly proportionally with the bin size. Indeed, now there are fewer data points per bin. Below I show two sets of the weights p_k for the same data set. The two probability distributions correspond to two different values of the bin width:



Clearly, in the limit of the vanishing bin size, the weights will vanish, too, at the same rate as the bin size does.

To handle this, let us remind ourselves the definition of the average of some function $f(x)$ over a set of data points:

$$(39) \quad \langle f(x) \rangle \equiv \frac{1}{N} \sum_i^N f(x_i)$$

When the number N of data is large, we may benefit from grouping the data into $M \ll N$ bins, just like we did it Chapter 2:

$$(40) \quad \langle f(x) \rangle \equiv \frac{1}{N} \sum_i^N f(x_i) = \sum_k^M \frac{N_k}{N} \tilde{f}(x_k) \equiv \sum_k^M p_k \tilde{f}(x_k)$$

where the index k labels bins and $\tilde{f}(x_k)$ is the value of $f(x)$ averaged over bin k . The weight $p_k \equiv N_k/N$ thus gives the partial quantity of the data falling within bin k , as before.

$$(41) \quad \langle f(x) \rangle = \sum_k^M \Delta x_k \frac{p_k}{\Delta x_k} \tilde{f}(x_k)$$

where where Δx_k is the width of bin k . Since the weight p_k scales linearly with Δx_k , the ratio $p_k/\Delta x_k$ remains finite in the $\Delta x_k \rightarrow 0$ limit and we are justified in defining the following function:

$$(42) \quad p(x) \equiv \lim_{\Delta x_k \rightarrow 0} \frac{p_k}{\Delta x_k}$$

called the *probability density*. It is the continuous analog of the discrete distribution function p_k . With this definition, the average in Eq. (43) can be rewritten as a definite integral:

$$(43) \quad \langle f(x) \rangle = \lim_{\Delta x_k \rightarrow 0} \sum_k^M \Delta x_k \frac{p_k}{\Delta x_k} \tilde{f}(x_k) = \int_{x_{\min}}^{x_{\max}} dx p(x) f(x)$$

where x_{\min} and x_{\max} delineate the range of the variable x . According to its definition (42), the function $p(x) = \frac{N_k}{\Delta x_k} N$ is the number of points per unit interval, times the total number of data N . Accordingly, the quantity $p(x)$ has dimensions of inverse x . In this sense, it is a probability *density*. Accordingly, when we average over the distribution, we integrate, not sum. Note that the probability density $p(x)$ is normalized to one, if the parent distribution p_k is:

$$(44) \quad \int_{x_{\min}}^{x_{\max}} dx p(x) = \lim_{\Delta x_k \rightarrow 0} \sum_k^M \Delta x_k \frac{p_k}{\Delta x_k} = \sum_k^M p_k = 1$$

One may say that the quantity $p(x) dx$ gives the partial quantity of data falling within the (infinitesimal) interval dx centered at x . One may also say that the function $p(x)$ is the *inverse* of the typical spacing between the data points $\Delta x_k/N_k$, times the total number of data N .

Because the quantity $p(x) dx$ vanishes for an infinitely narrow interval dx , one may say that the probability to for the variable x to have a precise value, say x_0 , is strictly zero. However, it is better to remember that the question of the probability to have a specific value is not well posed. When we have continuous distributions, we, instead ask questions like this: What is the probability for the variable x to be contained with an interval, say, $[x_1, x_2]$. This kind of question is answered by computing an integral:

$$(45) \quad p(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} p(x) dx$$

which could be thought of as counting all of the data within the $[x_1, x_2]$ of a histogram. As an example of using Eq. (45), consider finding the *median* x_m of a distribution. It is simply the value of the variable that splits the distribution exactly in two equal parts:

$$(46) \quad \int_{x_{\min}}^{x_m} p(x) dx = \int_{x_m}^{x_{\max}} p(x) dx = \frac{1}{2}$$

the last equation valid for distributions that are normalized to one. Although the median and the average of a distribution often follow each other, the median is sometimes preferable to the average, especially when the average does not even exist ($\int x p(x) dx = \infty$). The latter situations will not be encountered in this Course, but they do arise when the distribution in question has very long tails, i.e., the probability density decays to zero slowly. (It must decay to zero eventually, or else, it would not be normalizable.) Working with the median is often more convenient also when, for instance, the distribution is bimodal so that the values of the variable that are numerically close to the average of the distribution are not particularly representative of the distribution.

Similarly to the probability distribution for a single physical quantity, we can define a distribution density for more than one distributed variable at a time. For instance, one can define a two-variable probability density according to

$$(47) \quad p(x, y) \equiv \lim_{\Delta x_{k_1}, \Delta y_{k_2} \rightarrow 0} \frac{p_{k_1 k_2}}{\Delta x_{k_1} \Delta y_{k_2}}$$

One can then compute the average of any function of x and y by evaluating a double integral:

$$(48) \quad \langle f(x, y) \rangle = \iint dx dy p(x, y) f(x, y)$$

where we did not write out the integration limits for typographical clarity. When both the averaged function and the distribution factorize, the above integration reduces to a product of two 1D integrals:

$$(49) \quad \begin{aligned} \langle f_1(x) f_2(y) \rangle &= \iint dx dy p_1(x) p_2(y) f_1(x) f_2(y) \\ &= \left[\int dx p_1(x) f_1(x) \right] \times \left[\int dy p_2(y) f_2(y) \right] \end{aligned}$$

End of digression on Statistics.

The Gibbs-Boltzmann distribution is used to evaluate the probability of discretely distinct configurations (such as pregnant vs. not pregnant) and is not always straightforward to apply to situations where the variable labeling microscopic states seems to change continuously. This ambiguity is solved, more or less, in Quantum Mechanics. In the absence of a more rigorous treatment, we'll try to get away with consistency-type reasoning. For instance, we can use the Gibbs-Boltzmann distribution to write down the probability distribution for the coordinate and velocity of a particle moving in 1D subject to the potential $V(x)$:

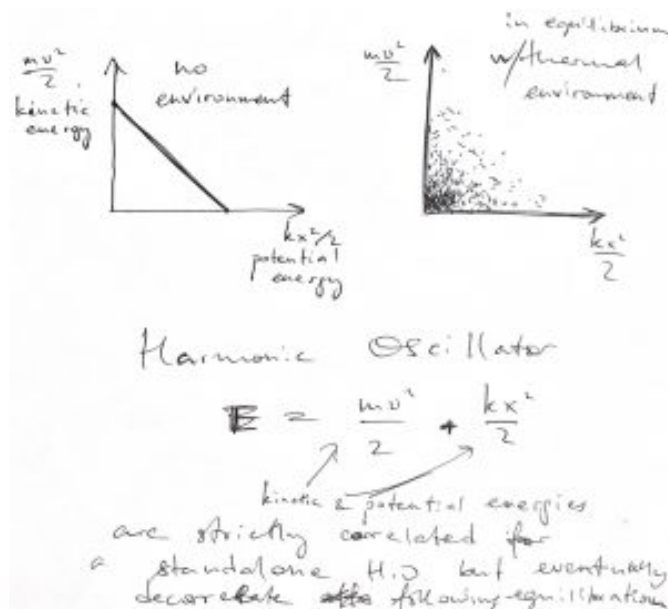
$$(50) \quad p(v, x) = C e^{-\beta[mv_x^2/2 + V(x)]}$$

because the energy of the particle is $E = mv_x^2/2 + V(x)$. We can reasonably guess that the constant C in front of the exponential must be independent of x . Indeed, shifting the potential over by length x_0 should simply shift the probability the distribution by the same length without multiplying it by some function of x_0 . The lack of dependence of C on v_x is a bit trickier. Here it helps to note that velocity changes, due to a non-vanishing force, do not explicitly depend on the velocity itself, according to Newton's 2nd law: $m\Delta v = \int f dt$, see also below.

In any event, Eq. (51) encodes the remarkable fact that in equilibrium, the coordinate and velocity are statistically independent! Indeed the distribution (51) factorizes into an x and v dependent part:

$$(51) \quad p(v_x, x) = C e^{-\beta[mv_x^2/2 + V(x)]} = C e^{-\beta mv_x^2/2} e^{-\beta V(x)}$$

Consider, for instance, with the harmonic oscillator, whose kinetic and potential energies exactly anti-correlate in the absence of interaction with an environment. Once exposed to a thermal environment, the two energies will eventually decorrelate, the relaxation time depending on the efficiency of momentum transfer from the oscillator to the environment.



Now, the x -dependent factor is sometimes called the Boltzmann distribution:

$$(52) \quad p(x) = A e^{-\beta V(x)}$$

where A is a normalization constant that has no x dependence.

An important example is the potential of the Earth's gravity as a function of height z , relatively to the ground:

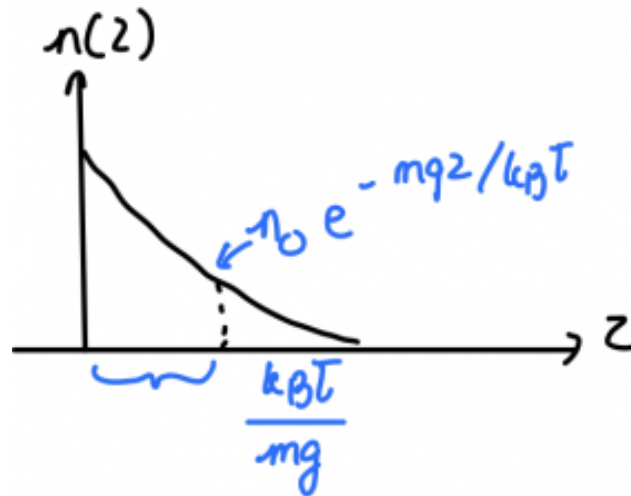
$$(53) \quad V(z) = m g z$$

It is easy to write down the resulting z -dependence of the concentration of a gas because by its very meaning, the concentration of a gas at a specific location is proportional to the probability for a gas molecule to be at that location:

$$(54) \quad n(z) = n(z)|_{z=0} e^{-mgz/k_B T}$$

where $n(z)|_{z=0}$ is the concentration near the ground.

We sketch this $n(z)$ below:



The exponential function decays very rapidly, the decay length in this particular case being determined by the quantity $k_B T / mg$. Thus the thickness of the atmosphere is determined by the very same quantity $k_B T / mg$. In reality, the temperature is not constant throughout the atmosphere and decreases quite rapidly with altitude, because of radiative cooling. As a result, the concentration profile will fall off with altitude even more rapidly as the isothermal, $T = \text{const}$ result would suggest. In any event, we arrive at a somewhat surprising result that the thickness of the atmosphere is determined not by the molecule's size—consistent with the molecules not being in contact much of the time—but by how fast the molecules move!

We have already written down the velocity dependent part of the distribution (23) of velocities, i.e. the Maxwell distribution, for 1D motion. Its functional form is that of so called Gaussian distribution (named after the mathematician Gauss):

$$(55) \quad p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

with $x_0 = 0$ and $\sigma = (k_B T / m)^{1/2}$. The distribution in Eq. (55) is also sometimes called the *normal* distribution and is incredibly important for this Course. You can convince yourself that the mean of the Gaussian distribution is given by

$$(56) \quad \langle x \rangle = x_0$$

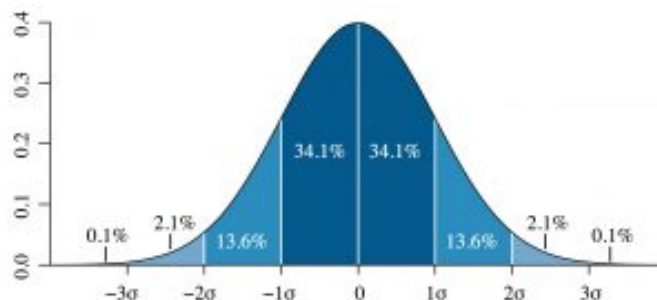
and variance

$$(57) \quad \langle (x - \langle x \rangle)^2 \rangle = \sigma^2$$

The variance $\langle (x - \langle x \rangle)^2 \rangle$ is also sometimes called the mean square deviation (msd), while its square root:

$$\begin{aligned} \Delta x &\equiv \langle (x - \langle x \rangle)^2 \rangle^{1/2} \end{aligned}$$

is called the root mean square deviation (rmsd), or the *standard deviation*. According to Eq. (57), the rmsd of the Gaussian distribution is numerically equal to the parameter σ , a very simple result. As can be seen in the picture below, the rmsd is a good measure of the width of the Gaussian distribution:



(By M. W. Toews. Own work, based (in concept) on figure by Jeremy Kemp, on 2005-02-09, [CC BY 2.5](#), [Link](#))

Indeed, we see that the $[-\sigma, \sigma]$ interval centered at the maximum x_0 of the distribution contains 68.2%, or so, of the data. A formal way to express this notion is: $\int_{x_0-\sigma}^{x_0+\sigma} p(x) dx \approx 0.682$.

Now, we note that the mean velocity in all directions is zero:

$$(58) \quad \langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$$

This was obvious beforehand since the gas, as a whole, is not moving anywhere.

We are now ready to write the velocity distribution for motion in 3D. Because the contributions of the translations in the three spatial directions to the total energy are *additive*:

$$(59) \quad \frac{m\langle v^2 \rangle}{2} = \frac{m\langle v_x^2 \rangle}{2} + \frac{m\langle v_y^2 \rangle}{2} + \frac{m\langle v_z^2 \rangle}{2}$$

the overall distribution for the three components v_x , v_y , and v_z is determined by simply multiplying together the respective three distributions:

$$(60) \quad p_{3D}(\vec{v}) = p(v_x)p(v_y)p(v_z) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta m v^2/2}$$

Note this distribution is isotropic, i.e., does not depend on the direction of the velocity vector, but only on its length. This is expected from the fact that all directions in space are equivalent, in the absence of external forces, and that the distributions of coordinates and velocities are decoupled in equilibrium, as already discussed. The above equation is also consistent with the lack of a velocity dependent pre-exponential factor in Eq. (23). If present, the resulting 3D distribution would not be isotropic! This was part of Maxwell's argument.

A good way of thinking about the distribution (60) is that the partial amount of particles whose velocities fall within the parallelepiped of dimensions $dv_x \times dv_y \times dv_z$ centered at the velocity $\vec{v} = (v_x, v_y, v_z)$ is equal to:

$$(61) \quad p_{3D}(\vec{v}) dv_x dv_y dv_z = p(v_x)p(v_y)p(v_z) dv_x dv_y dv_z$$

It is often convenient to ask, instead, the question: what is the distribution of *speeds*, not velocities? To answer this question, we note that all of the parallelepipeds contributing to a specific value of speed $v \equiv |\vec{v}| = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ comprise a spherical shell of some thickness dv centered at the origin. The volume of such a spherical shell is $4\pi v^2 dv$. Hence the distribution of the *speed* is

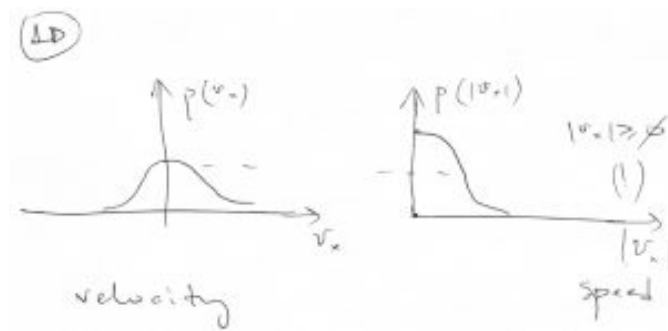
$$(62) \quad p(v) dv = p(v_x)p(v_y)p(v_z) 4\pi v^2 dv$$

yielding

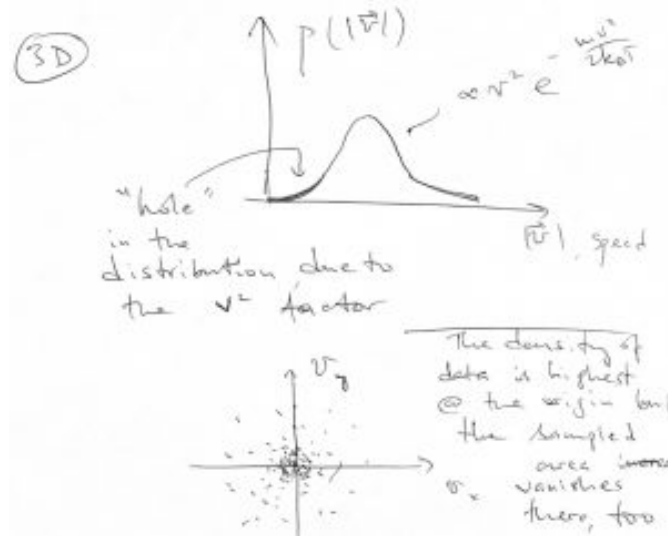
$$(63) \quad p(v) = 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} v^2 e^{-\beta m v^2/2}$$

Compare this with the distribution of speeds in 1D, which is obtained by simply “folding” together the negative and positive wings of the velocity distribution, since both v and $-v$ imply the same speed $|v|$:

$$(64) \quad p(v) = 2 \left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\beta m v^2/2}$$



Note the 3D speed distribution has a quadratic “hole” at the origin:



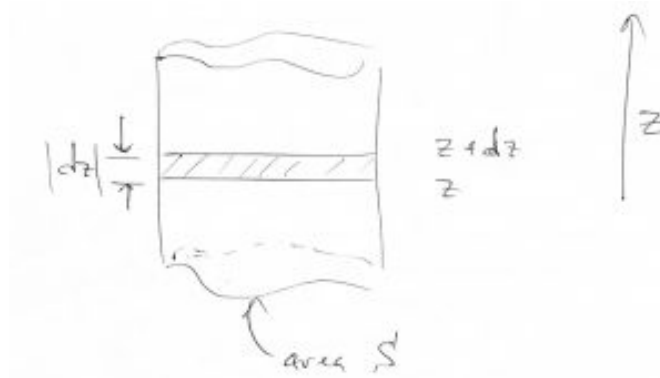
Likewise, the speed distribution will have a linear “hole” of the form $v e^{-\beta m v^2/2}$.

The “hole” comes about despite the value $\vec{v} = 0$ being the most likely value of the velocity. There is also a degeneracy of sorts, since in 3D, a whole shell of area $4\pi v^2$ contributes to the same value of $|\vec{v}|$.

(In 2D, the amount of degeneracy goes with the ring length $2\pi v$.)

Bonus discussion:

There is a rather vivid way to derive the Boltzmann distribution. Imagine a gas subject to gravity:



On the one hand, the pressure difference between the altitudes z and $z + dz$ should be exactly compensated by the weight of the gas contained within the layer:

$$p(z) - p(z + dz) = \frac{m g n S dz}{S} = m n g dz$$

where Sdz is the volume of the shaded region. Dividing by dz and taking the $dz \rightarrow 0$ limit yields

$$\frac{dp}{dz} = -mng$$

Yet according to the ideal gas law $p = nk_B T$, and so

$$\frac{dn}{dz} = -\frac{nmg}{k_B T}$$

Solving the differential equation yields:

$$n(z) = n(z)|_{z=0} e^{-\frac{mgz}{k_B T}}$$

Finally, we have seen that there are two ways to think about thermal phenomena. Mathematicians prefer to think in terms of probabilities. When two events are uncorrelated, the probability of the compound event factorizes: $p = p_1 \times p_2$. Chemists and physicists often prefer to think in terms of energies or energy-like quantities. In this case, statistical independence, or lack of interaction between events reveals itself through additivity of energies. The two ways are essentially equivalent, the connection understood through the properties of the mathematical functions e^x and $\ln x$: $p = p_1 \times p_2 \propto e^{-\beta(E_1 + E_2)}$ or, equivalently, $E = E_1 + E_2 = -k_B T (\ln p_1 + \ln p_2) + \text{const} = -k_B T \ln(p_1 \times p_2) + \text{const} = -k_B T \ln p + \text{const}$.

6.

Entropy, Thermodynamic Potentials, Free energy, Heat, Work, Laws of Thermodynamics

We showed in the last Chapter that when the Maxwell distribution is written for the speed—as opposed to the velocity—the characteristic exponential $e^{-\beta mv^2/2}$ becomes multiplied by a factor that depends on the speed v , in dimensions 2 and 3. Formally, this comes about because in spatial dimensions greater than one, to a specific value of the *speed*, there corresponds a large number of possibilities in terms of the velocity, the possibilities corresponding to distinct *directions* of motion, i.e. the angular orientation of the velocity vector. (In 1D the situation is not very interesting; there are only two directions and, hence, only two possibilities.) Moreover, the number of the possibilities increases with the value of the speed because the number of end points for the velocity vector goes as $4\pi v^2 dv$ in 3D and $2\pi v dv$ in 2D. This sort of “degeneracy”, where to a single value of the variable of interest there may correspond more than one distinct microstate was a direct result of us using a reduced description. Indeed, instead of using a full description in terms of the three components of the velocity (in 3D), we now opt to use a smaller number of variables—one, to be precise—the speed. Thus we no longer monitor the direction of motion. Another, related example is the energy levels of a hydrogen atom, where we know the number of distinct electronic states whose principle quantum number is equal to n , scales as $2 \times n^2$. For instance, for $n = 2$ (which is the valence shell for the elements from the 2nd period of the Periodic Table) there are 4 orbitals altogether: 1 s orbital and 3 p orbitals. For each one of those $(1 + 3) = 4 = 2^2$ orbitals, the electronic spin can be directed either up or down. Hence, the degeneracy is $2 \times 2^2 = 8$. (Note this n^2 degeneracy is directly related to the v^2 degeneracy of the Maxwell distribution of 3D speeds we just discussed.)

We saw in the last example that to a particular value of energy, there may correspond a number of distinct microstates that differ by the value of some other physical quantity. (For the hydrogen atom example, that other physical quantity is the angular momentum, something we will discuss in the 2nd part of the Course.) In some cases, we will choose not to monitor that other quantity, for whatever reason. And in some cases, monitoring most microscopic variables is simply impractical because of the sheer quantity of the microstates at a given value of energy, implying a vast amount of degeneracy. In fact, one expects that the degeneracy, call it Ω , scales exponentially with the system size. As a simple illustration, imagine covering a flat floor with square tiles. Assume that all the tiles are identical in size while each tile has an irregular, non-symmetric pattern drawn on it so that there are 4 distinct ways to orient each tile. If there are N tiles altogether, clearly there are $\Omega = 4^N$ distinct configurations. But $4^N = e^{N \ln 4}$, i.e., the degeneracy scales exponentially with the system size N . This is a good toy model to have in mind when we think about of large collections of molecular dipoles or vibrations of atoms in solids.

There is also another, subtler kind of degeneracy: The aforementioned tiles are identical, as mentioned, but can still be distinguished and labeled by their location, the same way even identical particles can be labelled by their location, if the particles are part of a solid and can not readily exchange positions. But fluids and gases are different: Here the constituent molecules can exchange places on time scales much shorter than the experimental time scale. In such cases, we can only monitor a single parameter, i.e., the mass density at a specific locale, not the actual identity of the many particles; this is a great example of a reduced description. How large is the degeneracy resulting from this reduction in the number of degree of freedom we can monitor? The multiplicity of distinct permutations of objects in a large set, which physically correspond to the objects exchanging places, scales very rapidly with the system size, faster than exponentially, in fact. For instance, the number of distinct ways to place N distinct objects in N slots is $N \times (N - 1) \times (N - 2) \times \dots \times 2 \times 1$

. Indeed, there are N options for the 1st object since there are N available slots, there $(N - 1)$ options for the 2nd object, since one slot is already occupied, and so on. We see that the number of permutations is equal to the *factorial* function: $N! \equiv N \times (N - 1) \times (N - 2) \times \dots \times 2 \times 1$. But, according to Stirling's approximation, $N! \approx e^{N \ln N - N}$ for large N . Clearly, $e^{N \ln N}$ grows more rapidly than e^{CN} for sufficiently large N , if C is a constant independent of N . Counting such degeneracies becomes much harder when interactions are present. Yet in many cases, one may still be able to infer them retroactively using measured macroscopic quantities and then making conclusions about the microscopics. This is an important aspect of Thermodynamics.

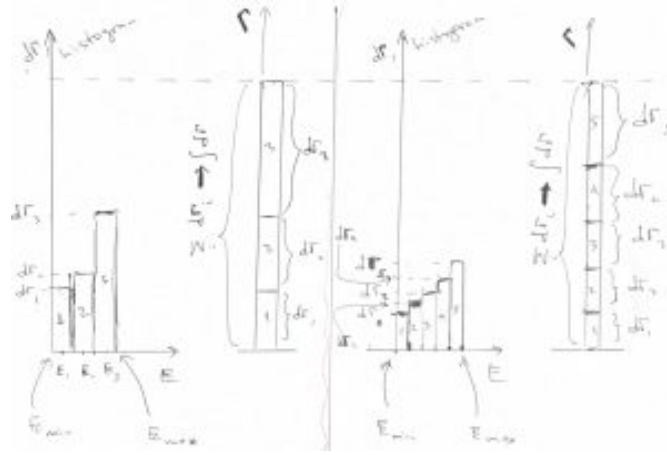
Huge multiplicities of states at a given value of energy are characteristic of most macroscopic systems; the corresponding situations will be our primary focus in the Thermo part of the Course. The large degree of degeneracy implies one can expect the energy values to cover the allowed energy range rather densely, which, then, compels one to bin those energy values using very narrow bins:

$$\begin{aligned}
 \text{number } d\Gamma(E) \text{ of microstates } i \text{ such that } E - \frac{dE}{2} \leq E_i < E + \frac{dE}{2} \\
 &= \sum_{i, E - \frac{dE}{2} \leq E_i < E + \frac{dE}{2}} 1 \\
 (1) \qquad &\equiv \Omega(E) dE
 \end{aligned}$$

where, by construction, the bins fully cover the allowed energy range and do not overlap. The quantities $d\Gamma(E)$ are, thus, simply the heights of the bars on the histogram of the possible energy values of the system. Let us elaborate on the notation $d\Gamma(E)$, which might come across as confusing. The argument E indicates that the height $d\Gamma$ of each bar on the histogram generally depends on the value of the energy E the bar is centered on. The letter d in front of Γ indicates that in the limit of a vanishing bin width, the quantity $d\Gamma(E)$ scales linearly with dE the same way the number of data N_k scaled linearly with the bin width Δx_k in our discussion of continuous probability distributions in the last Chapter. In contrast with the last Chapter, however, the probability density is normalized not to one, but to the total number states are accessible in principle:

$$\begin{aligned}
 \int \Omega(E) dE &\equiv \int d\Gamma(E) = \Gamma(E_{\max}) - \Gamma(E_{\min}) \\
 (2) \qquad &= \Gamma(E_{\max}), \text{ total number of microstates}
 \end{aligned}$$

Here we observe that using d in front of Γ has an added advantage: In the limit of infinitely many bins—whose width must become infinitely small, then—the sum of the bins becomes a continuous integral. Think of $\Gamma(E)$ as the total height of the histogram bars, counting from the left up to the point E , stacked on top of each other. (Note $\Gamma(E)$ is an example of the so called cumulative probability distribution.) If we change the precise way to break up our energy range into intervals dE , the height of individual bars changes, too, but the total height does not change because it is equal to the total number of data, i.e., the the number of the microstates. Below we illustrate this point by using two distinct ways to histogram the same distribution, using 3 and 5 bins, respectively.



This picture indicates, among other things, that the bars become thinner and shorter at the same time, while the height-to-width ratio stays essentially constant and depends only on the location of the bar. According to Eq. 1, this ratio is equal to the function $\Omega(E)$ itself:

$$(3) \quad \Omega(E) = \lim_{dE \rightarrow 0} \frac{d\Gamma(E)}{dE}$$

Note the function Ω is, thus, not only the derivative of Γ , but also the *density of states* because it gives the number of states per energy interval!

(If the notation $d\Gamma(E)$ is still confusing, consider a simple function $f(x) = x^2$. Then $df(x) \equiv d(f(x)) = d(x^2) = 2x dx$. Consequently, $df(x)/dx = 2x$ is simply the derivative of the function $f(x)$ with respect to its argument x . To obtain $d(x^2) = 2x dx$, we do this: $d(x^2) \equiv (x + dx)^2 - x^2 = 2x dx + (dx)^2$ and then drop the $(dx)^2$ term because it can be made arbitrarily smaller than the $2x dx$ term in the limit $dx \rightarrow 0$.)

Once histogrammed according to their respective values of energy, the microstates lose all their identifiers other than the energy itself. Thus, two states within a single bin are no longer distinguished, in our description. In this way, the description is a reduced one. Yet this apparent sacrifice enables one to greatly simplify bookkeeping the accessible states, since now one can rewrite the discrete sum for the number of accessible states as a continuous integral:

$$(4) \quad Z \equiv \sum_i e^{-\beta E_i} = \int d\Gamma(E) e^{-\beta E} = \int dE \frac{d\Gamma(E)}{dE} e^{-\beta E} = \int dE \Omega(E) e^{-\beta E}$$

Note that the infinite temperature limit of Z is simply the total number of states Γ : $Z(\beta = 0) = \Gamma(E_{\max})$, that is, all of the microstates become equally likely and, thus, automatically accessible.

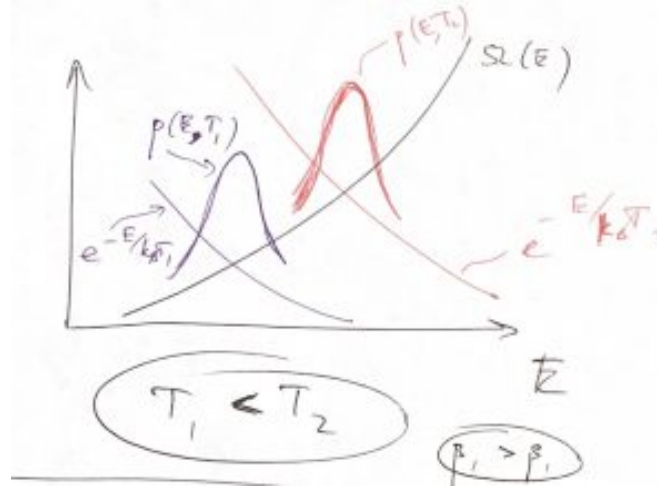
Now, the integrand in Eq. (4), $\Omega(E) e^{-\beta E}$, is clearly the probability distribution for the energy:

$$(5) \quad p(E) = \Omega(E) e^{-\beta E}$$

This distribution is not normalized to one, but, instead to the number of accessible states, per Eq. (4):

$$(6) \quad \int dE p(E) = Z$$

The maximum of the probability distribution $p(E)$ then determines the most probable value of the energy, a quantity of considerable interest. As illustrated in the picture below, this maximum is determined by an interplay between the rapidly increasing function $\Omega(E)$ and the rapidly decreasing function $e^{-\beta E}$.



Physically, $\Omega(E)$ is an increasing function of energy because at higher energies, particles move faster and can get closer together, implying there is more available space, effectively. The decrease of the factor $e^{-\beta E}$, on the other hand, apparently indicates that borrowing energy from the environment becomes harder as the temperature is lowered: The lower the temperature, the greater the β , the faster the factor $e^{-\beta E}$ decays with E .

We have seen that the degeneracy $\Omega(E)$ is expected to scale exponentially or faster with the system size N and thus it will be convenient to introduce a new function $S(E)$, called the *entropy*:

$$(7) \quad \Omega(E) \equiv \frac{1}{\delta E} e^{S(E)/k_B}$$

where we introduced a pre-exponential factor $1/\delta E$ of dimensions inverse energy to account for the fact that the quantity Ω as defined in Eq. (1) has dimensions of inverse energy. By construction, the quantity δE depends on the system size N more slowly than the exponential part $e^{S(E)/k_B}$. According to the definition above, one may think of the entropy as the logarithm of the number of states:

$$(8) \quad S(E) \equiv k_B \ln[\Omega(E) \delta E]$$

We use the Boltzmann constant k_B in the definition of entropy for historical reasons. Sometimes this historical artifact makes life more convenient and sometimes it is a nuisance, but there is no deep physics there. The entropy is, fundamentally, a dimensionless quantity which we obtain by taking the logarithm of a *number*. A more rigorous argument is quite obtuse and is beyond the scope of this course, but it should be immediately clear that the quantity δE has dimensions of energy and, furthermore refers to the total energy of the system. (In fact, it reflects the magnitude of energy variations.) Thus δE scales at most linearly with the system size N or more slowly. This is much slower than the exponential dependence of $\Omega(E)$ on N and so δE can be neglected in most cases of interest. Thus, we can write:

$$(9) \quad S(E) = k_B \ln[\Omega(E)]$$

while being mindful that, strictly speaking, this equation is incorrect dimensions-wise and there is an omitted additive contribution that would have restored the correct dimensions. In contradistinction with the common—also misleading and overused—notation that the entropy is a measure of disorder, it is best thought of as a measure of diversity or multiplicity of states at a given value of energy.

A remarkable feature of the entropy is that it is *additive* for non-interacting systems. Indeed, the total number of states for a compound system made of uncorrelated sub-systems 1 and 2 is simply the product of the respective numbers of states:

$$(10) \quad \Omega(E) = \Omega_1(E_1) \Omega_2(E_2)$$

where we should take care to note that the total energy of two non-interacting systems is the sum of the energies of the individual sub-systems:

$$(11) \quad E = E_1 + E_2$$

Taking the logarithm of this equation and multiplying by k_B yields, in view of Eq. (9), that

$$(12) \quad S(E) = S_1(E_1) + S_2(E_2)$$

This equation (or its equivalent in Eq. (10) is yet another manifestation of the statistical independence of uncorrelated systems, which does not explicitly refer to specific microstates but, instead, only to their energies. Eq. (12) is thus generally distinct from the more basic equation $g(E_{k_1}^{(1)} + E_{k_2}^{(2)}) = g(E_{k_1}^{(1)}) \times g(E_{k_2}^{(2)})$ we wrote earlier for the individual contributions of microstates to the accessible number of states. No less important is the implication that according to Eq. (12), the entropy is an *extensive variable*, i.e. it *scales linearly with the system's size* N . Indeed, suppose the subsystems 1 and 2 are identical. Thus the compound system is simply twice bigger. At the same time, its entropy is twice larger than that of an individual sub-system, according to Eq. (12). For the very same reason, the energy is *also* an extensive quantity, see Eq. (11).

In view of the entropy's definition, (9), we can rewrite Eq. (4) in a rather revealing form:

$$(13) \quad \begin{aligned} Z &= \int dE e^{-\beta[E - TS(E)]} \\ &\equiv e^{-\beta \tilde{A}(E, T)} \end{aligned}$$

where we have defined a new, energy-like quantity:

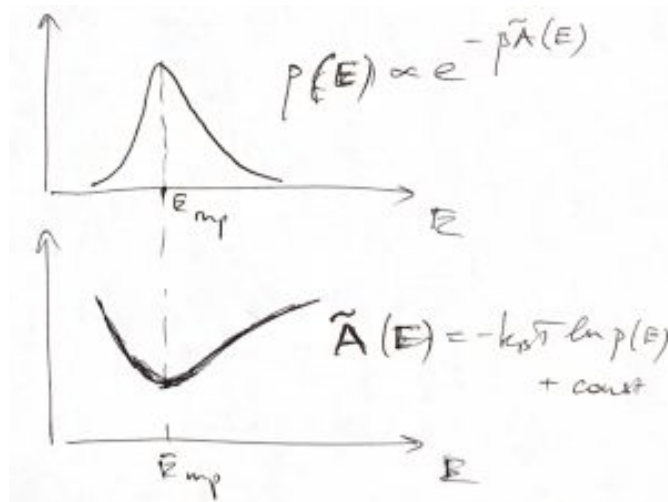
$$(14) \quad \tilde{A}(E) \equiv E - TS(E)$$

and we keep in mind, that in addition to the energy E , the function $\tilde{A}(E)$ also depends on the temperature T , volume, the particle number, and, possibly, other quantities.

Now the probability distribution for energy values can now be written in a rather simple fashion:

$$(15) \quad p(E) \propto e^{-\beta \tilde{A}(E)}$$

Because the function e^{-x} is a monotonically decreasing function of its argument, the maximum of the probability $e^{-\beta \tilde{A}(E)}$ is located exactly at the minimum E_{mp} of the function $\tilde{A}(E)$. Thus the problem of finding the likeliest value of the energy, at some fixed value of temperature and volume, etc., is reduced to finding the minimum of the energy-like quantity $\tilde{A}(E)$.



Furthermore, after comparing the quantity $e^{-\beta \tilde{A}(E)}$ with the Boltzmann distribution for a particle subject to a potential energy $\mathcal{V}(x)$:

$$(16) \quad p(x) \propto e^{-\beta \mathcal{V}(x)}$$

we conclude that the function $\tilde{A}(E)$ plays the role of a potential energy for the energy of the system itself! (Isn't that fascinating?) For this reason, it can be called a *thermodynamic potential*. Furthermore, the most probable value of the energy corresponds with the *equilibrium* position of the thermodynamic potential $\tilde{A}(E)$. Thus we have a license to vividly think of thermodynamic equilibrium as a mechanical equilibrium with respect

to *thermodynamic* potentials. We will see soon, that similar thermodynamic potentials can be written down for other important thermodynamic quantities such as the volume or the chemical composition of a reactive mixture. The possibility of writing such thermodynamic potentials for quantities of interest is, arguably, the most important outcome of Thermodynamics. Note that those quantities are not even dynamical variables! But it gets even more interesting from here.

By how much should we expect the energy to fluctuate around its most likely value? Let us Taylor expand our thermodynamic potential around E_{mp} up to the second order in deviation of the energy from its most probable value E_{mp} :

$$\begin{aligned}
 \tilde{A}(E) &\approx \tilde{A}(E_{\text{mp}}) + \left. \frac{\partial \tilde{A}}{\partial E} \right|_{E=E_{\text{mp}}} (E - E_{\text{mp}}) + \frac{1}{2} \left. \frac{\partial^2 \tilde{A}}{\partial E^2} \right|_{E=E_{\text{mp}}} (E - E_{\text{mp}})^2 \\
 &= \tilde{A}(E_{\text{mp}}) + \frac{1}{2} \left. \frac{\partial^2 \tilde{A}}{\partial E^2} \right|_{E=E_{\text{mp}}} (E - E_{\text{mp}})^2
 \end{aligned}
 \tag{17}$$

where in the 2nd equation we took account of the fact that the first derivative of a function vanishes at a minimum: $\left. \frac{\partial \tilde{A}}{\partial E} \right|_{E=E_{\text{mp}}} = 0$. We recall that the Taylor expansion is a way to approximate complicated functions using a relatively simple functional form, i.e, a polynomial. The narrower the involved interval of the argument, the lower order polynomial is needed to achieve a given accuracy. By construction, discarding terms of order $(E - E_{\text{mp}})^3$ and higher implies that we are approximating our function by a parabola.

Substituting Eq. (17) into Eq. (15) yields

$$p(E) \approx \frac{1}{\delta E} e^{-\beta \tilde{A}(E_{\text{mp}})} e^{-\frac{\beta}{2} \left. \frac{\partial^2 \tilde{A}}{\partial E^2} \right|_{E=E_{\text{mp}}} (E - E_{\text{mp}})^2}
 \tag{18}$$

This, then, shows that the probability distribution of the energy is a Gaussian distribution where, we see, the variance is proportional to the inverse 2nd derivative of $\tilde{A}(E)$ at the minimum:

$$\sigma^2 = \left(\frac{\beta \partial^2 \tilde{A}}{\partial E^2} \right)^{-1}_{E=E_{\text{mp}}}
 \tag{19}$$

Let us focus, for a moment, on the scaling of the *variance* of the energy distribution with the system size N . We already noted that the energy scales linearly with the system size thus allowing one to define the energy per particle $\varepsilon \equiv E/N$, which is an *intensive* variable that carries no information whatsoever about the system size. Thus,

$$(20) \quad E = N \varepsilon$$

Likewise, we can define the intensive analog of the quantity \tilde{A} :

$$(21) \quad \tilde{A} = N \tilde{a}$$

because \tilde{A} is an extensive quantity, being the sum of two extensive quantities: E and $-TS(E)$. Hence we infer that the variance of the energy scales linearly with the system size:

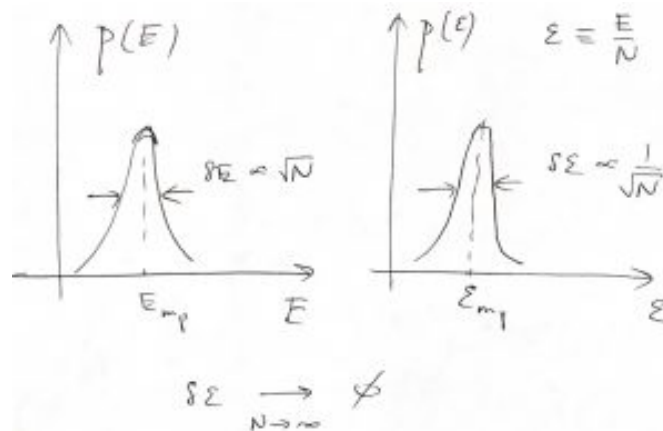
$$\sigma^2 = \left(\frac{\partial^2 \tilde{A}}{\partial E^2} \right)^{-1}_{E=E_{\text{mp}}} = N \left(\frac{\partial^2 \tilde{a}}{\partial \varepsilon^2} \right)^{-1}_{\varepsilon=\varepsilon_{\text{mp}}}
 \tag{22}$$

This is an incredibly important result because it shows that the rmsd of the energy from its most probable value scales only as a *square root* of the system size:

$$(23) \quad \delta E = \sigma \propto \sqrt{N}$$

Consequently, the relative magnitude of the energy fluctuation scales inversely with \sqrt{N} and, thus, can be made arbitrarily small given a sufficiently large system:

$$(24) \quad \frac{\delta E}{E_{\text{mp}}} \propto \frac{1}{\sqrt{N}}$$

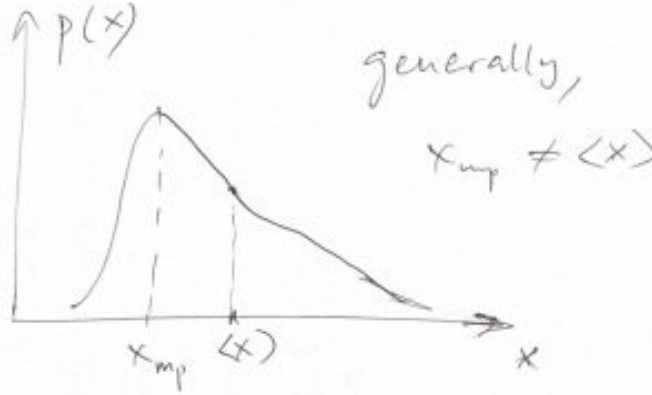


Thus we observe that in a practically important limit of large systems— N could be as large as 10^{23} —the probabilistic description above becomes essentially deterministic, since the intensive properties become sharply defined. To put this in perspective, let us estimate the chances that the energy per particle deviates, say, by $0.001\% = 10^{-5}$ from its most probable value for a system containing one mole of particles. Typically, $\epsilon \sim k_B T$, up to a numerical factor of order one. We will learn soon that $(\partial^2 \tilde{A} / \partial E^2)^{-1} = C_V T$, where C_V is the heat capacity at fixed volume. This means that at constant volume, $\delta E = \sqrt{C_V k_B T^2}$. The heat capacity is typically k_B or less, per particle. Thus the reduction in the probability, off its largest value,
$$e^{-(E-E_{\text{mp}})^2 / 2(\delta E)^2} \sim e^{-N(\epsilon-\epsilon_{\text{mp}})^2 / 2(C_V/N)k_B T^2} = e^{-6 \times 10^{23} \times (10^{-5})^2 / 2} =$$
 is $e^{-3 \times 10^{13}} \sim 10^{-10^{13}}$, a monstrously small number that has 10^{13} zeros, or so, after the decimal point. Conversely, if you happened to witness such a deviation, your chances of observing it again are essentially zero. There are important consequences of this rapid falloff in the probability:

1. If a very large system happens to be in equilibrium, which minimizes the pertinent thermodynamic potential, it will remain in equilibrium. (The precise identity of the thermodynamic potential depends on the specifics of the experiment and will be discussed as we proceed.) Conversely, if the system happens to be away from equilibrium—for instance, because we had temporarily imposed a constraint and then let go—it will *spontaneously and irreversibly* evolve toward equilibrium, so as to minimize the pertinent thermodynamic potential, and then, again, will stay there forever. This is the essence of the 2nd Law of Thermodynamics, which essentially says that the most probable process will occur with probability one.
2. For systems that are not too large, fluctuations of thermodynamic variables off their most likely values are noticeable, however, are usually small. Since the quadratic expansion of thermodynamic potentials, such as that in Eq. (17), approximates the potential well in a small range, the statistics of thermodynamical variables are subject to the Gaussian distributions. The maximum of the distribution is located at the minimum of the corresponding thermodynamic potential, as in Eq. (17). The width of the distribution is determined by curvature (2nd derivative) of the thermodynamic potential, as in Eq.

(19).

3. Because the most probable value and the average value for the Gaussian distribution coincide, we conclude that the expectation value of a thermodynamic variable corresponds to its equilibrium value, i.e., the value that minimizes the corresponding thermodynamic potential. This is not simply a formal remark. On the contrary, the mean and the most probable value of a distribution are generally not equal to each other (though often are numerically close), see Figure below. Thus in the rest of the Thermo part of the Course, we will use the terms “average” and “most probable” interchangeably, while being mindful that it is the average, i.e., expectation value of a quantity that is measured in an experiment.



That the fluctuations of extensive quantities should scale with \sqrt{N} is as important as it is somewhat nonintuitive. Indeed, why should it be that a quantity whose value is so large, i.e., proportional to the particle number N itself, should have fluctuations that are much smaller? The answer to this is that in a sufficiently large system, separate parts behave sufficiently independently so that their fluctuations are not correlated and, hence, will largely cancel out when added together.

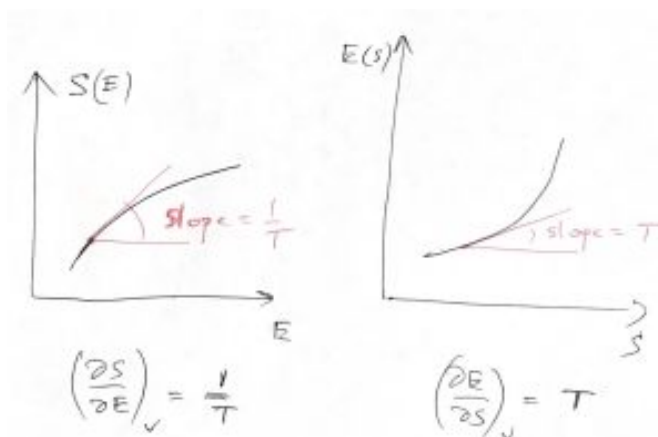
Let us now write out a necessary condition for the minimum of the thermodynamic potential \tilde{A} , where it is understood that \tilde{A} is a function of three variables: E , T , and V , and we are keeping the temperature and volume constant:

$$(25) \quad \frac{\partial}{\partial E} \tilde{A} = \frac{\partial}{\partial E} [E - T S(E, V)] \Big|_{E=E_{\text{mp}}} = 1 - T \left(\frac{\partial S}{\partial E} \right)_V \Big|_{E=E_{\text{mp}}} = 0$$

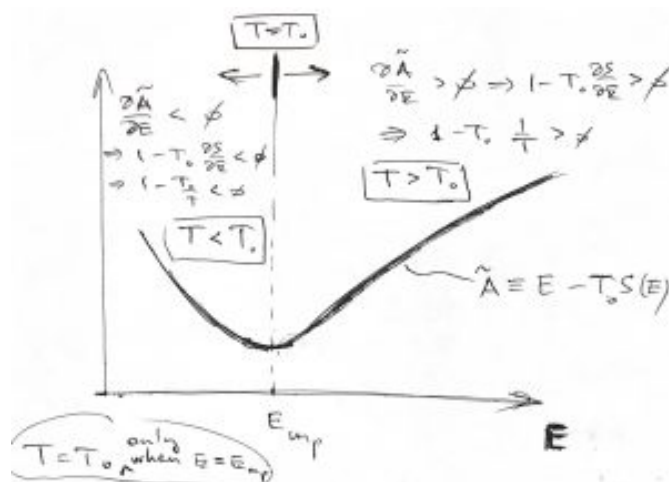
The explicit volume dependence of \tilde{A} is exclusively through the entropy, $S = S(E, V)$, which we have indicated. Since the minimum of \tilde{A} corresponds with equilibrium, the above equation yields that the *equilibrium* value of the energy and the temperature are not independent but, instead, inter-relate via the following constraint:

$$(26) \quad \left(\frac{\partial S}{\partial E} \right)_V \Big|_{E=E_{\text{mp}}} = \frac{1}{T}$$

Here we also explicitly indicate that the volume is being kept constant. Because of this dependence, we use the partial derivative with respect to E in Eq. (26). This equation can be interpreted in, essentially, two ways. On the one hand, suppose we know that our system is, in fact, equilibrated while being at a certain value of energy E_0 . Then, Eq. (26) tells us that the temperature must be equal to the derivative $\frac{\partial S}{\partial E}$ taken exactly at point $E = E_0$. In this way of doing things, the temperature T is a function of the expectation value of the energy:



(It is also a function of volume V , because the entropy S is a function of both E and V .) On the other hand, suppose we bring our system in contact with a much larger system whose temperature is T_0 . What happens if the system's energy is, say, lower than its equilibrium value? Then $\partial \tilde{A} / \partial E < 0$, which implies $1 - T_0(\partial S / \partial E) < 0$ or, by virtue of Eq. (26), that $T < T_0$. This is consistent with the definition of temperature! Indeed, since the volume and particle number are kept constant, the only way for the system to receive energy is via heat exchange. Thus the inequality $T < T_0$ is consistent with fact that the heat will flow to the system so as to enable it to increase its energy until it reaches its equilibrium value, at which point $T = T_0$.



The case of the system's having initially a higher than the equilibrium value of energy is entirely analogous.

In contrast with independent variable E , the *equilibrium* value of the energy is constrained by Eq. (26) and is now a function of temperature T and volume V :

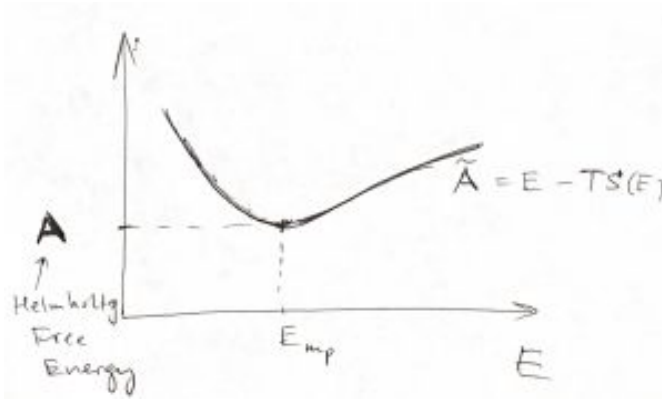
$$(27) \quad E_{\text{mp}} = E_{\text{mp}}(T, V)$$

The same applies to the *equilibrium* value of entropy:

$$(28) \quad S(T, V) = S[E_{\text{mp}}(T, V), V]$$

where we recapitulated that the entropy $S = S(E, V)$ from Eq. (7) may depend on the volume explicitly, and now, also through $E_{\text{mp}}(T, V)$.

Now, note that the equilibrium value of the function \tilde{A} is, in fact, is the minimum value of \tilde{A} . We now define the **Helmholtz free energy** as this equilibrium, minimum value of \tilde{A} :



We reiterate that the quantity \tilde{A} is a function of three variables, i.e., E, V, T . In contrast, the Helmholtz free energy is a function of only two independent variables, because of the constraint imposed by Eq. (26), which thus eliminates one degree of freedom. By virtue of Eqs. (27) and (28), a natural (but not unique) choice of those two independent variables is temperature and volume:

$$(29) \quad A(T, V) \equiv \tilde{A}(E_{\text{mp}}(T, V), T, V) = E_{\text{mp}}(T, V) - TS[E_{\text{mp}}(T, V), V]$$

where we used Eq. 14. From this moment on, we will consider exclusively equilibrium configurations. To simplify notations, we will drop the “mp” label:

$$(30) \quad E_{\text{mp}} \rightarrow E$$

It is also worthwhile to streamline Eq. (29)

$$(31) \quad A \equiv E - TS$$

Now consider a small increment of both sides of Eq. (31):

$$(32) \quad (dA)_V = (dE)_V - d(TS)_V = (dE)_V - [S(dT)_V + T(dS)_V]$$

where, in the usual way, we retain only quantities that are first order in the increment and discard higher order terms because they can be made arbitrarily smaller by decreasing the magnitude of the increment: $d(xy) \equiv (x + dx)(y + dy) - xy = xdy + ydx + dxdy \approx xdy + ydx$.

Eq. (32) can be greatly simplified after we recall that the temperature can be regarded as a function of the equilibrium value of the energy: $E = E_{\text{mp}}(T) \Rightarrow T = T(E)$ or, equivalently, of the equilibrium value of the entropy, see the Figure following Eq. (26). It is, then, convenient to re-write Eq. (26) here in an equivalent form:

$$(33) \quad T = \left(\frac{\partial E}{\partial S} \right)_V$$

This way, E and T are regarded as functions of the variables S and V and we are varying the variable S , in Eq. (33), while keeping the volume V constant.

One can rewrite Eq. (33) profitably as

$$(34) \quad (dE)_V = TdS$$

which says that the energy increment in a slow isochoric process is simply the entropy increment times the temperature. (“Isochoric”=“taking place at constant volume”.) The reason we must specify that the process be slow is that past Eq. (29), we have limited ourselves to processes where the energy (and all other quantities) are at their equilibrium values.

Eqs. (33) and (32) then readily yield

$$(35) \quad (dA)_V = -S(dT)_V \text{ or, equivalently, } S = - \left(\frac{\partial A}{\partial T} \right)_V$$

We have seen that the free energy is extremely useful as its value is directly tied to the probability of the corresponding thermodynamic state. Yet the entropy S , the energy E , and the Helmholtz free energy A are not directly measured in experiment. Let us, then, further elaborate on the physical meaning of these thermodynamic

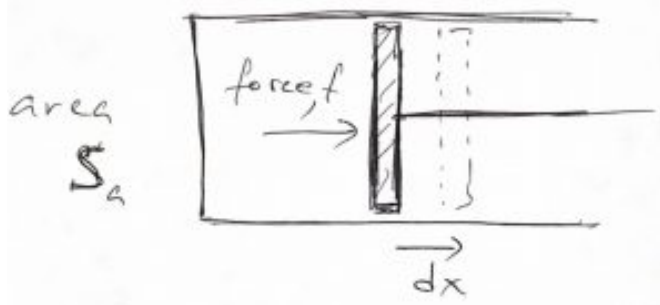
functions and the implications of the present formalism for experiment. To do so, we will invoke a physical law while also explicitly considering changes in the *volume*. The physical law in question is the law of conservation of energy. In the present context, this law states that changes in the system's energy, if any, can result from either heat exchange or work performed by the system:

$$(36) \quad dE = \delta Q - \delta W \quad \leftarrow \text{"The 1st Law"}$$

where δQ is the amount of heat the system has received or given up during the process in question, while δW is the work performed by the system. It suffices to note for now that the symbols d and δ indicate that we are considering small amounts; their precise meaning will be clarified later. As stated above, the law of conservation of energy is referred to as the **First Law of Thermodynamics**.

As already alluded to in Chapter 2, breaking up the full energy change into contributions due to heat exchange and work, respectively, is empirical and, admittedly, somewhat artificial. Informally speaking, we divide the processes behind the energy/momentum exchange between our system and its environment into those processes that we cannot directly see or control (heat exchange) and those that we can, in fact, directly see and control (work). This way of doing things was inevitable in the early days, when advanced microscopy was unavailable, but remains incredibly useful to this day and will remain so for the foreseeable future; we can "see" a lot more these days but individually controlling huge numbers of degrees of freedom will remain impossible. In any event, because of the empirical nature of Eq. (36), we should remain careful. For instance, if one want to consider work in the absence of heat exchange, one must remember that there is no perfect way to thermally insulate a system and so a $\delta Q = 0$ process is an idealization that is adequate on short enough times scales such that relatively little heat exchange has occurred. On the other hand, those short times should still be longer than the relaxation time of the system, if we want to use results developed under the assumption of equilibrium. This is rarely a problem in practice, since mechanical equilibration often occurs on time scales that are shorter than characteristic times of heat exchange, a notable exception represented by convection processes, such as those leading to hurricanes.

Above said, let us write down an expression for the performed work. According to the picture below:



one can evaluate the work done by the system as

$$(37) \quad \delta W = f dx = \frac{f}{S_a} S_a dx = p dV$$

where $p = f/S_a$ is our old friend *pressure*, not probability (!). A more general argument that applies to arbitrary geometries can be found in the CHEM4370 notes. In addition to providing an explicit expression for the work, the above equation shows that no work is performed if there are no volume changes, something we already knew. Thus we obtain

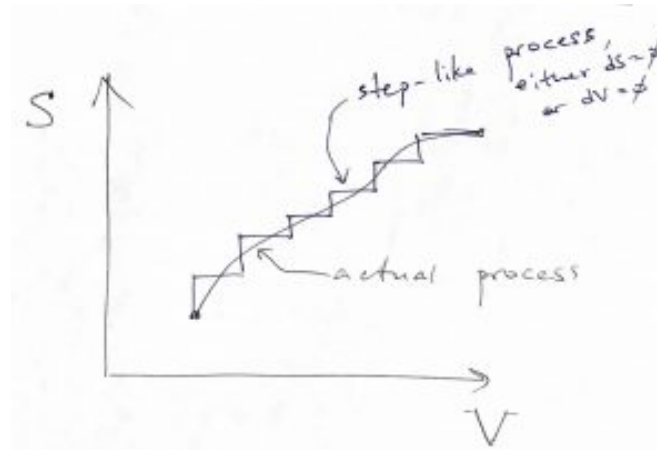
$$(38) \quad (dE)_V = \delta Q$$

a statement made without explicit reference to the time scale of the experiment. We now compare this equation with Eq. (34), which was written for slow processes, and notice that the right hand sides of the two equations do not contain an explicit reference to whether the process is isochoric or not and, thus, should be equal to each other under general circumstances, so long as the conditions for the individual equations are met. Thus we obtain that for slow processes, such that the system can be regarded as equilibrated at any given time, there is one-to-one correspondence between heat exchange and entropy changes:

$$(39) \quad \delta Q = T dS$$

A somewhat less Jesuitical way to show that Eq. (39) applies to arbitrary non-isochoric processes connecting

two states with *different* volumes, it is helpful to approximate the actual process by a step-like process of the kind depicted below:



and notice that entropy changes will be collected only along those legs of the process where the volume stays constant. By taking the limit of an infinitely small step size, we can make the values of any quantity, such as the temperature or pressure etc., along the jagged path to be arbitrarily close to that for the actual, smooth path. As a side note, here we explicitly take advantage of the fact that in equilibrium, the energy and temperature (and all other thermodynamics quantities) are true functions of two variables, entropy and volume in this case. (There is a third variable, the particle number N , but we are keeping it constant throughout this Chapter.) Thus the value of energy is fully determined by specifying S and V , irrespective of what the energy value was at earlier times. Indeed, the energy is what they call a *state function*. We will see in due time that heat and work are not state functions, hence our using δ , not d in Eq. (36).

Eq. (39) drives home the statistical foundation of Thermodynamics. On the one hand, entropy reflects the number of degrees of freedom that we chose not to control or could not control in principle. On the other hand, that heat has to do precisely with molecular motions, which we cannot control individually in principle. We can only control some of the *average* characteristics of those motions, such as the average kinetic energy.

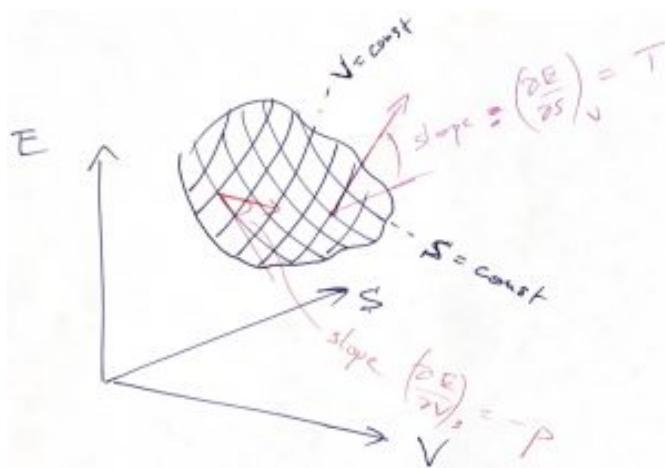
Thus we obtain that for slow, or *quasistatic* processes such that the system can be regarded as equilibrated at all times:

$$(40) \quad dE = TdS - p dV$$

In other words, if during some (elemental) slow process, the entropy underwent a change dS and volume dV , then one can immediately evaluate the resulting change in the energy, if the temperature and pressure are known. In fact, the temperature specifies the rate of change of energy with entropy at constant volume, while the negative pressure specifies the rate of change of energy with volume at constant entropy:

$$(41) \quad \begin{aligned} T &= \left(\frac{\partial E}{\partial S} \right)_V \\ -p &= \left(\frac{\partial E}{\partial V} \right)_S \end{aligned}$$

Indeed, the top equation is obtained by setting $dV = 0$ ($V = \text{const}$) in Eq. (40) and dividing by dS , while the bottom equation is obtained by setting $dS = 0$ ($S = \text{const}$) and dividing by dV . This can be illustrated graphically:



Eq. (40) may well be the most consequential equation of the Course, as far as its quantitative implications are concerned. (The equation will be later generalized to cases when we allow the particle number to change, as would be necessary, for instance, in Thermochemistry.) The first thing to do is to obtain a differential of the Helmholtz free energy $A \equiv E - TS$:

$$(42) \quad dA = d(E - TS) = dE - TdS - SdT$$

which, by virtue of Eq. (40), leads to a simple result:

$$(43) \quad dA = -SdT - p dV$$

or, equivalently,

$$(44) \quad \begin{aligned} -S &= \left(\frac{\partial A}{\partial T} \right)_V \\ -p &= \left(\frac{\partial A}{\partial V} \right)_T \end{aligned}$$

What is the significance and use of Eqs. (41) and (44) for practical applications? In the ideal turn of events, one can calculate the density of states $\Omega(E, V)$ and, thus, evaluate $S(E, V) = k_B \ln \Omega(E, V)$. One then solves this for the energy as a function of entropy and volume $E = E(S, V)$. Next, one uses Eq. (41) to calculate the temperature and pressure as functions of entropy and volume: $T = T(S, V)$ and $p = p(S, V)$. Now we have four quantities— T , S , p , and V —and two equations connecting them, implying only two of those quantities are independent. This means that we can predict, in principle, the pressure as a function of volume and temperature and thus predict the *equation of state*: $p = p(V, T)$. To be clear, the dependences $V = V(p, T)$ and $T = T(V, p)$ are also called equations of state. Given the $p(V, T)$ dependence is known, one can then calculate important response functions, such as the isothermal compressibility:

$$(45) \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad \leftarrow \text{isothermal compressibility}$$

or its inverse, called the bulk modulus

$$(46) \quad \kappa_T = -V \left(\frac{\partial p}{\partial V} \right)_T \quad \leftarrow \text{bulk modulus}$$

These quantities are of utmost importance in materials science as they reflect how compressible/stiff the material is. Note the factors in front of the derivatives are needed to make these important response functions intensive quantities. In other words, we are talking about relative, not absolute volume changes. Another important response function is the thermal expansion coefficient:

$$(47) \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \leftarrow \text{thermal expansivity}$$

which tells one how much the object will expand or contract as the temperature changes. For instance, chemical glassware is made of quartz, not ordinary window glass because the latter has too large an expansion coefficient. As a result, washing a hot beaker with cold water would create large strains and result in its breaking.

If, on the other hand, one uses the relations $T = T(S, V)$ and $p = p(S, V)$ to express the entropy as a function of temperature and volume: $S = S(T, V)$, one can readily evaluate the heat capacity at constant volume:

$$(48) \quad C_V \equiv \left(\frac{\delta Q}{\delta T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad \leftarrow \text{heat capacity at constant volume}$$

and, likewise, the heat capacity at constant pressure:

$$(49) \quad C_p \equiv \left(\frac{\delta Q}{\delta T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad \leftarrow \text{heat capacity at constant pressure}$$

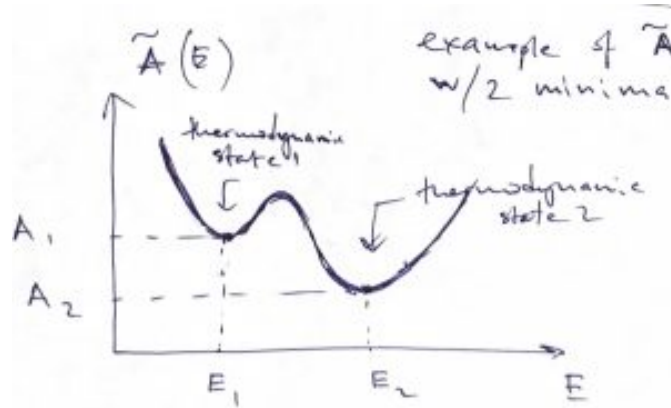
Alternatively, if one can evaluate the Helmholtz free energy as a function of temperature and volume, $A = A(V, T)$, one may infer the entropy and pressure using Eq. (44) and follow the rest of the program as just described. In practice, it is often mathematically easier to go the Helmholtz route, which is called the “canonical” formalism. (The $S(E)$ centered formalism is often referred to as “microcanonical”.) The key notion here is that after one substitutes the Gaussian approximation for the probability density (18) into Eq. (6) and integrates, one obtains: $Z = \frac{\sqrt{2\pi\sigma^2}}{\delta E} e^{-\beta A}$, where used Eq. (29). The pre-exponential factor scales only algebraically, i.e. as a power, with the system size, while the exponential scales exponentially, which is a much much faster dependence. Thus, to a leading order in N , the Helmholtz energy is related to the partition function Z in a very simple way:

$$(50) \quad Z = e^{-\beta A}$$

or

$$(51) \quad A = -k_B T \ln Z$$

An interesting corollary of Eq. (50) is that if the system has more than one stable or metastable states and so one can define a Helmholtz free energy for each minimum, as in the Figure below:



then the probability of being in the thermodynamic state 1 relative to the thermodynamic state 2 is simply the exponential of the free energy difference times $(-\beta)$:

$$(52) \quad \frac{Z_1}{Z_2} = \frac{e^{-\beta A_1}}{e^{-\beta A_2}} = e^{-\beta(A_1 - A_2)}$$

We reiterate that each of the thermodynamic states 1 and 2 is generally a vast ensemble of microstates

characterized by some value of energy. The number of *accessible* microstates is given by the quantity Z . The probability ratio for two distinct thermodynamic states is given by the ratio of the respective numbers of the states accessed by the system, hence Eq. 52. After we compare the result in Eq. 52 to the probability ratio of two *microstates*: $p_1/p_2 = e^{-\beta(E_1-E_2)}$, we conclude that when one cannot control the identity of the microstate, but can only control the average value of the energy—by bringing the system in contact with an environment—the relevant probabilities are determined not by the energy itself but, instead, by the *free* energy. Often, what we regard as distinct “thermodynamic states” refer to distinct phases or physical states with distinct properties, such as a folded and unfolded protein molecule, respectively. In view of Eq. (31), the probability ratio from Eq. 52 becomes

$$(53) \quad \frac{Z_1}{Z_2} = \frac{e^{S(E_1)/k_B}}{e^{S(E_2)/k_B}} e^{-\beta(E_1-E_2)} = \frac{\Omega(E_1)}{\Omega(E_2)} e^{-\beta(E_1-E_2)}$$

i.e., in the presence of multiplicity of microstates at a particular value of energy, the distribution of energy is determined by that multiplicity, in addition to the Boltzmann weight $e^{-\beta E}$, as we saw already in the last Chapter. We have now generalized those early ideas to apply to rather arbitrary structures of energy levels. Per Eq. 52, two thermodynamic states are equally likely, at fixed volume and temperature, when their Helmholtz energies are mutually equal:

$$(54) \quad A_1 = A_2 \text{ for two states in equilibrium}$$

which, then, provides a criterion for things like the folding transition of a protein. In turn, this means

$$(55) \quad E_1 - TS_1 = E_2 - TS_2$$

We observe an important pattern: If one state is stabilized in terms of energy, then the other state should have a higher entropy.

Note that per Eq. (31), the energy and free energy become equal at $T = 0$, i.e. when the molecular motions stop. These are the motions that are responsible for the degeneracy, in the first place. Accordingly, $A = E$ at any temperature, if the energy levels are non-degenerate, $S = 0$, i.e., there are no degrees of freedom we are not explicitly controlling.

Why the *free* energy? We can integrate Eq. (40) at constant entropy ($S = \text{const}$, $dS = 0$), to see that the work performed by the system in the absence of heat exchange is given by the decrease in the energy:

$$(56) \quad \Delta E_S = \int_1^2 (dE)_S = - \int_1^2 p dV$$

This is analogous to our earlier statement that the work of a conservative force is the negative of the change of the potential:

$$(57) \quad \Delta \mathcal{V} = \int_1^2 d\mathcal{V} = - \int_1^2 f dx$$

In contrast, integration of Eq. 43 at constant temperature ($T = \text{const}$, $dT = 0$) shows that the work performed by the system that exchanges heat with the environment, so as to maintain its temperature, is given by the decrease in the *free* energy:

$$(58) \quad \Delta A_T = \int_1^2 (dA)_T = - \int_1^2 p dV$$

On the other hand, at constant temperature, $\Delta A_T = \Delta(E - TS)_T = \Delta E - T\Delta S$. The system performs useful work only when it expands, so that $p dV > 0$. This generally implies an increase in the entropy and, hence, $\Delta A_T = \Delta E - T\Delta S < \Delta E$. Thus we conclude that if the system exchanges heat with environment, so as to keep its temperature steady, the amount of useful work a system can perform is lowered. The energy stored in the molecular motions is not harnessed, consistent with our earlier statement on the inability to control microstates. Thus, semantically, the word “free” in the free energy refers to energy *available* to do useful work. Also, note the formal similarity of how the decrease in the energy and free energy relate to the

performed work, Eqs. (56) and (58) respectively, to how the decrease in the potential energy relates to the work of a conservative force, Eq. (57). This similarity provides another justification for the term “thermodynamic potential”.

Now, the number of accessible states $Z = Z(T, V)$, which is an explicit function of temperature and volume, is usually (but not always!) easier to compute than $S = S(E, V)$. For this reason, the canonical formalism is often preferred for calculations. Yet a quality evaluation of Z from scratch is often hard, too. But sometimes, the equation of state and calorimetric data are already known, for instance from experiment. (Calorimetry has to do with measuring the heat capacity.) It is then possible to extract the free energy from that information and other quantities of interest using the present description as a formal framework. We will illustrate this hybrid approach here for the ideal gas, since we do happen to know its equation of state:

$$(59) \quad pV = Nk_B T$$

Since we do not have—as of yet—an expression for the entropy, neither of the equations (41) and (44) suffice to determine the free energy. However, we do have some access to the calorimetry since we know the temperature dependence of the energy. It is simply the number of particles times $k_B T/2$ times the number of degrees of freedom $n_{\text{d.o.f.}}$:

$$(60) \quad E = N \frac{k_B T}{2} n_{\text{d.o.f.}}$$

We can express this through the standard heat capacity, by first setting $dV = 0$ in Eqs. (40), then dividing the resulting equation by dT and using Eq. (48). This yields

$$(61) \quad C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Differentiating Eq. (63) with respect to temperature, then, yields the following expression the heat capacity at constant volume, per particle:

$$(62) \quad c_V = \frac{C_V}{N} = \frac{k_B}{2} n_{\text{d.o.f.}}$$

while the energy of the gas can expressed through the heat capacity and temperature according to:

$$(63) \quad E = C_V T \equiv N c_V T$$

The full heat capacity is a sum of three contributions: translational, rotational, and vibrational. Here is a table that summarizes these three contributions:

	c_V						
translation, 3D	$\frac{3k_B}{2}$						
rotation	<table border="1"> <tr> <td>atom</td><td>0</td></tr> <tr> <td>linear molecule</td><td>k_B</td></tr> <tr> <td>molecule, not linear</td><td>$\frac{3k_B}{2}$</td></tr> </table>	atom	0	linear molecule	k_B	molecule, not linear	$\frac{3k_B}{2}$
atom	0						
linear molecule	k_B						
molecule, not linear	$\frac{3k_B}{2}$						
vibration, per themally active degree of freedom, $k_B T > \hbar\omega$	k_B						

To obtain an actual expression for the entropy as a function of temperature and volume, we first re-write Eq. (40)

$$(64) \quad dS = \frac{1}{T}dE + \frac{p}{T}dV$$

and then substitute $dE = C_V dT$, as obtained by taking an increment of Eq. (63), and $\frac{p}{T} = \frac{Nk_B}{V}$, per the equation of state of the ideal gas:

$$(65) \quad dS = C_V \frac{dT}{T} + Nk_B \frac{dV}{V}$$

This expression is very easy to integrate between any two states characterized by distinct values of the two variables, T and V , because they enter in the r.h.s. separately. Let's take for the initial and final states for the integration, respectively, some standard reference state, labeled using the superscript " \ominus " and the state at the actual temperature and volume:

$$(66) \quad S(T, V) - S(T^\ominus, V^\ominus) = C_V \ln \left(\frac{T}{T^\ominus} \right) + Nk_B \ln \left(\frac{V}{V^\ominus} \right)$$

Note the result of the integration is expressly independent of the integration path, consistent with the the entropy being a state function. We will not proceed with explicitly calculating the Helmholtz free energy quite yet, since using Eq. 43 as the knowledge of the entropy will suffice for now.

We now return to the **2nd Law of Thermodynamics**. We have seen that for a large system, the likeliest set of configurations will be realized with essentially probability 1. We have also seen that the notion of maximizing the probability, a statistical concept, is interchangeable with the notion of minimizing an appropriate thermodynamic potential, a mechanical notion. Specifically, when the volume and temperature are fixed, the equilibrium energy value is determined by the minimum of the function

$$(67) \quad \tilde{A}(E, V, T) \equiv E - T S(E, V)$$

Conversely, any configuration other than that minimizing the function $\tilde{A}(E, V, T)$ would not be equilibrium. To create such a configuration, one would have to impose some additional constraints. Such additional constraints, by definition, imply that the number of accessible configurations at a given value of E is now decreased. This effectively means a smaller value of $S(E, V) = k_B \ln \Omega(E, V)$ and a larger value of \tilde{A} , by Eq. 67. Thus one can formulate the 2nd law of Thermodynamics in the following ways:

1. The entropy of a large, isolated system can only increase, and cannot decrease over time. It reaches its maximum value in equilibrium.
2. At constant volume and temperature, the Helmholtz free energy of a large system can only decrease, and cannot increase. It reaches its minimum value in equilibrium.

A word on thermodynamic stability. The constraint (26) on the equilibrium values of energy and temperature only guarantees that the function \tilde{A} —or the probability distribution $p(E)$ —is at its extremum. But we actually want a *maximum* for $p(E)$ and, hence, a minimum for \tilde{A} . It is thus required that the second derivative of \tilde{A} at $E = E_{\text{mp}}$ be positive. This way the extremum will be a stable minimum, not an unstable maximum or a configuration in neutral equilibrium. Therefore we must require that

$$(68) \quad \left. \frac{\partial^2 \tilde{A}}{\partial E^2} \right|_{E=E_{\text{mp}}} > 0$$

where, note, T and V are kept constant. In view of Eq. 14 and the fact that $T \equiv 3\langle mv^2/2 \rangle / k_B > 0$, this condition yields

$$(69) \quad \left(\frac{\partial^2 S}{\partial E^2} \right)_V < 0, \text{ at } E = E_{\text{mp}}$$

and note that $S(E)$ in this equation is a function of E and V only. We have seen, however, that the derivative $(\partial S/\partial E)_V$ at any value of E is equal to the inverse temperature at that *same* value of E , and so

$$(70) \quad \left(\frac{\partial^2 S}{\partial E^2} \right)_V \equiv \left(\frac{\partial(\partial S/\partial E)_V}{\partial E} \right)_V = \left(\frac{\partial(1/T)}{\partial E} \right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_V = -\frac{1}{C_V T^2}$$

where we used the chain rule of differentiation and that $d(1/T)/dT = -1/T^2$, and also Eq. 61. Thus we obtain a stability condition for thermal fluctuations:

$$(71) \quad C_V > 0$$

It is easy to convince ourselves that if this condition is not satisfied, we would have an instability on our hands. Indeed, a negative heat capacity would imply a *maximum* in the \tilde{A} function, which, in turn, would lead to an absurd situation: As the energy of the system becomes increasingly less than the “equilibrium” value at the extremum of \tilde{A} , its temperature increases which lead to the system giving away the energy and a further decrease in the energy. This is a case of an effective force that is not restoring, but, on the contrary, pushes one away from the equilibrium point. This corresponds to an unstable equilibrium, of course.

We conclude by stating the **3rd Law of Thermodynamics**. It states that the entropy must vanish at zero temperature:

$$(72) \quad S(T = 0) = 0$$

This law is obeyed by most systems for reasons that will become more clear in the Quantum part of the Course. Here we only note that owing to Eqs. 61 and 71, the energy must be a monotonically increasing function of temperature. Thus the energy reaches its minimum value at $T = 0$. The 3rd law, then, essentially implies that the ground state of a physical system is not degenerate, i.e., $\Omega = e^{N^\alpha}$, where $\alpha < 1$. And so the entropy per particle, $\frac{S}{N} = \frac{\ln \Omega}{N} = N^{\alpha-1}$ vanishes in the infinite system limit $N \rightarrow \infty$. There are a few seeming counterexamples to the 3rd Law, but most physical systems of interest in this Course do obey this law. In turn, it provides for a helpful (though not mandatory) way to define a standard state for the entropy.

7.

Gibbs Free Energy, Entropy of Mixing, Enthalpy, Chemical Potential, Gibbs-Duhem

Next we determine the thermodynamic potential that controls the equilibration of the volume, in addition to controlling the equilibrium value of the energy. In many, of not most cases of interest, the volume of the system cannot be rigidly controlled. Instead, we can only be sure of the value of the pressure. For instance, most liquids do not fill their container fully, and so even if the container is completely rigid (which is an idealization) and fully sealed, the liquid will occupy only a portion of the container, the rest occupied by its vapor or the corresponding crystal. In an open container, clearly one can only control the pressure.

Perhaps the easiest way to determine the pertinent thermodynamic potential is to first write down the energy conservation law in a form that brings out the energy and volume dependence of the entropy:

$$(1) \quad dS = \frac{1}{T}dE + \frac{p}{T}dV$$

We are mindful that the above equation pertains to the *equilibrium* values of all the quantities. Thus in equilibrium,

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

$$(2) \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}$$

and, hence,

$$(3) \quad 1 - T \left(\frac{\partial S}{\partial E}\right)_{V,N} = 0$$

$$(4) \quad p - T \left(\frac{\partial S}{\partial V}\right)_{E,N} = 0$$

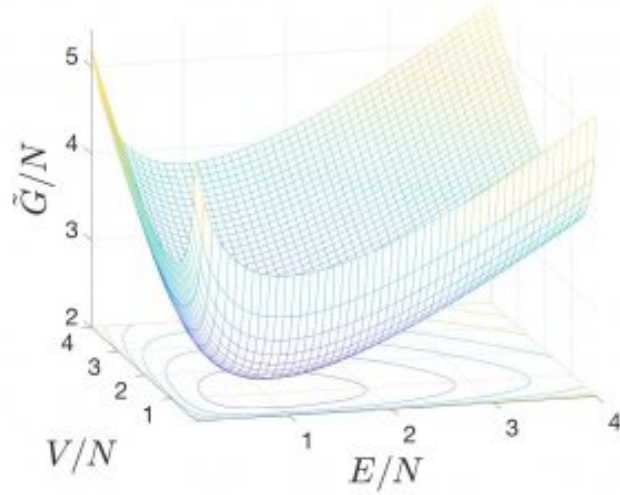
Note we have explicitly indicated that the particle number N is being kept constant, which will be of use later one.

Recall that Eq. 3 resulted from minimizing the function $\tilde{A} \equiv E - TS(E, V)$ with respect to E . It is not hard to see that Eq. 3 results just as well from minimization with respect to E of the following function

$$(5) \quad \tilde{G} \equiv E + pV - TS(E, V, N)$$

At the same time, we can readily convince ourselves that minimizing this function with respect to V also yields Eq. 4! To be clear, the parameters T and p are kept constant during the minimization as well. The function \tilde{G} , then, represents the sought thermodynamic potential governing the fluctuations of both the energy and volume when the temperature and pressure are externally imposed. Just as for the thermodynamic potential \tilde{A} , there are two ways to interpret Eq. 2: On the one hand, they tell us the values of temperature and pressure that are needed

to achieve specific equilibrium values for the energy and volume. On the other hand, given specific values of externally imposed temperature and pressure, the equilibrium energy and volume correspond to the minimum of the function \tilde{G} , where Eq. 2 expresses the formal condition for the location of the minimum on the \tilde{G} surface. As an example, we show the \tilde{G} surface for the ideal gas:



where we used the expression

$$(6) \quad S(E, V, N) - S^\ominus = N c_V \ln \left(\frac{E}{N c_V T^\ominus} \right) + N k_B \ln \left(\frac{V}{V^\ominus} \right)$$

obtained by taking the $S(V, T, N)$ dependence derived in the last Chapter:

$$(7) \quad S(T, V) - S(T^\ominus, V^\ominus) = C_V \ln \left(\frac{T}{T^\ominus} \right) + N k_B \ln \left(\frac{V}{V^\ominus} \right)$$

and substituting $C_V = N c_V$ and $T = E/C_V = E/(N c_V)$. Note we must use the entropy as a function of energy, volume, and particle number $S = S(E, V, N)$ for both \tilde{A} and \tilde{G} ! In the graph, we set $T = 1$ and $p = 1$ and note that the precise choice of S^\ominus , T^\ominus , and V^\ominus affects only the vertical, but not the lateral position of the graph. Thus, the positions of the minima are not affected. Lastly, it is convenient to graph things so that all of the extensive properties, if any, are given per particle.

In the situation where T and p stand for externally imposed temperature and pressure and we are considering fluctuations of energy and volume, it is easy to see that such fluctuations will be subject to a restoring force if the curvature of the \tilde{G} surface is positive throughout. We have already discussed the stability with respect to energy fluctuations in the preceding Chapter and postpone further discussion of the necessary criteria until the next Chapter.

Similarly to how we defined the Helmholtz free energy as the minimum of the \tilde{A} potential, we now define the **Gibbs free energy** as the minimum of the \tilde{G} function:

$$(8) \quad \begin{aligned} G &\equiv \tilde{G}(E_{\text{mp}}(T, p, N), V_{\text{mp}}(T, p, N), T, p, N) \\ &= E_{\text{mp}}(T, p, N) - T S[E_{\text{mp}}(T, V), V_{\text{mp}}(T, p, N), N] + p V_{\text{mp}}(T, p, N) \end{aligned}$$

or, simply,

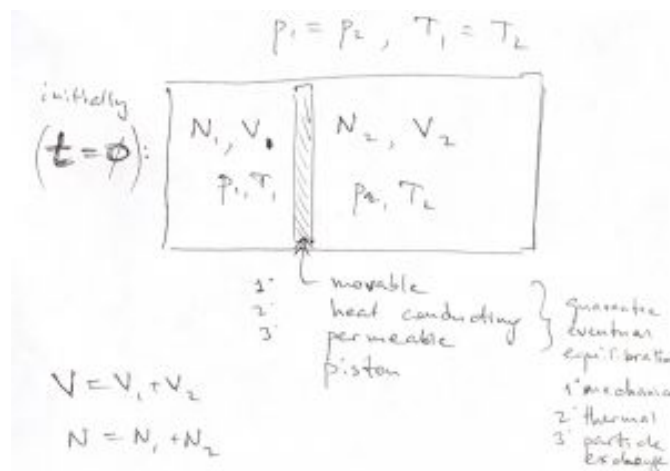
$$(9) \quad G \equiv E - T S + p V$$

where it is understood that every quantity is at its equilibrium value and, as such, is a function of exactly three independent quantities. A natural—but not unique!—choice of the variables is T , p , and N .

We are now ready to formulate yet another version of the 2nd Law of Thermodynamics, i.e., that at constant

pressure and temperature, a large system will spontaneously and irreversibly relax so as to minimize its Gibbs free energy. Once equilibrated, the system will remain in equilibrium indefinitely. This form of the 2nd Law is particularly useful because $T, p = \text{const}$ conditions are particularly common in experiment. To avoid confusion, we point out that although the equilibration of the system is all but inevitable, the 2nd Law, by itself, does not provide guidance as to the *kinetics* of the equilibration. These kinetics may, in fact, be rather slow. For instance, the stable form of solid carbon at normal conditions is graphite, not diamond. Yet diamond is incredibly stable, as we all know. Likewise, liquid glycerol can be stored on the shelf for decades, at normal conditions, yet its stable form at normal conditions is a crystalline solid!

As a simple yet useful illustration of the utility of the $p, T = \text{const}$ form of the 2nd Law, let us convince ourselves that gaseous mixtures essentially never de-mix. Imagine two distinct, nearly ideal gases occupying two sides of a container separated by a movable, thermally conducting partition. The partition is also weakly permeable to both gases. Note these properties guarantee eventual equilibration: mechanical, thermal, and with respect to particle exchange. Suppose the gases occupy volumes V_1 and V_2 and are maintained at the same temperature and pressure.



Thus, according to the ideal gas law, the particle numbers must be proportional to the respective volumes:

$$(10) \quad \frac{N_1}{N_2} = \frac{V_1}{V_2}$$

Thus the mole fractions of the two gases are, respectively

$$(11) \quad x_1 \equiv \frac{N_1}{N_1 + N_2} = \frac{V_1}{V_1 + V_2}$$

and

$$(12) \quad x_2 \equiv \frac{N_2}{N_1 + N_2} = \frac{V_2}{V_1 + V_2}$$

Note $x_1 + x_2 = 1$.

Clearly, both the thermal and mechanical equilibrium are in place, but the system is not in full equilibrium: Since the concentrations of each gas differ on the opposite sides of the partition, there will be uncompensated fluxes of both kinds of particles until the mixture will have the same composition in both parts of the container. No quantity in Eq. 9 will change as a result of the particle exchange except for one: the entropy. As a result of the mixing, the volume of gas 1 will increase from V_1 to $(V_1 + V_2)$ and the volume of gas 2 will increase from V_2 to V . The resulting entropy change is, then,

$$\begin{aligned}
\Delta S_{\text{mix}}/k_B &= \left[N_1 \ln \left(\frac{V_1 + V_2}{V^\ominus} \right) + N_2 \ln \left(\frac{V_1 + V_2}{V^\ominus} \right) \right] \\
&- \left[N_1 \ln \left(\frac{V_1}{V^\ominus} \right) + N_2 \ln \left(\frac{V_2}{V^\ominus} \right) \right] \\
&= \left[N_1 \ln \left(\frac{V_1 + V_2}{V_1} \right) + N_2 \ln \left(\frac{V_1 + V_2}{V_2} \right) \right] \\
&= (N_1 + N_2) \left[\frac{N_1}{N_1 + N_2} \ln \left(\frac{V_1 + V_2}{V_1} \right) + \frac{N_2}{N_1 + N_2} \ln \left(\frac{V_1 + V_2}{V_2} \right) \right]
\end{aligned}
\tag{13}$$

In terms of the mole fraction x and the total particle number $N \equiv N_1 + N_2$, this expression looks particularly appealing:

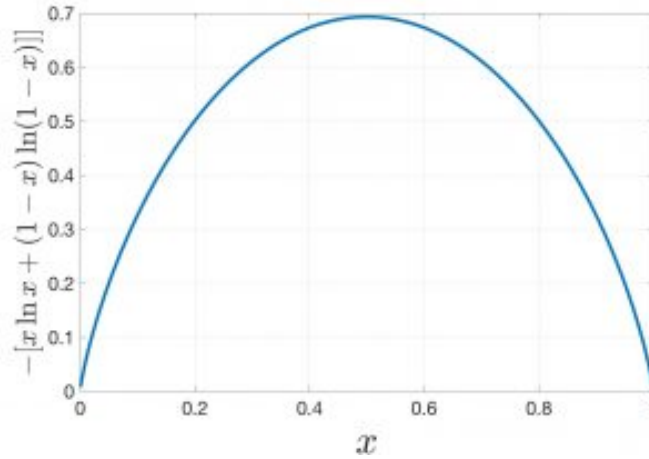
$$(14) \quad \Delta S_{\text{mix}}/k_B = -N(x_1 \ln x_1 + x_2 \ln x_2)$$

One can likewise derive that for an arbitrary mixture of ideal gases,

$$(15) \quad \Delta S_{\text{mix}}/k_B = -N \sum_i x_i \ln x_i$$

a celebrated formula, due to Gibbs.

One can easily convince oneself that the mixing entropy is always *positive*, which we will do here graphically for the binary mixture from Eq. 14 while remembering that $x_2 = 1 - x_1$. The mixing entropy vanishes only for pure substances, $x_1 = 0$ or $x_2 = 0$, of course and is maxed out at $k_B \ln 2$ per particle for an equal mixture $x_1 = x_2 = 1/2$:



The corresponding Gibbs free energy change is, then, always negative:

$$(16) \quad \Delta G_{\text{mix}} = -T S_{\text{mix}} < 0$$

To appreciate just how unlikely de-mixing would be, we compare the probability of the mixed vs. de-mixed state. As in the preceding Chapter, the ratio of the numbers of accessible states is given by the exponential of the free energy times (β) , the pertinent free energy being is that due to Gibbs, because we are keeping fixed temperature and pressure:

$$(17) \quad \frac{Z_{\text{mix}}}{Z_{\text{de-mix}}} = e^{-\beta \Delta G_{\text{mix}}} = e^{S_{\text{mix}}/k_B}$$

For one mole worth of a 50/50 mixture this would yield $\sim e^{4 \cdot 10^{23}} \sim 10^{10^{23}}$, a grotesquely large number. To put this in perspective, I quote here the well known French mathematician Borel (by way of G.N.Lewis's book "The anatomy of Science"): "Imagine a million monkeys allowed to play upon the keys of a million typewriters. What is the chance that this wanton activity should reproduce exactly all of the volumes which are contained in the library of the British Museum? It certainly is not a large chance, but it may be roughly calculated, and proves in fact to be considerably larger than the chance that a mixture of oxygen and nitrogen will separate into the two pure constituents."

Now, the aforementioned choice of the quantities T , p , and N as the arguments of G is natural not only in view of the definition of the Gibbs energy as the minimum of the \tilde{G} function at fixed p , T , and N , but also because of the fact that the partial derivative of G w.r.t. these variables are particularly simple. To discuss this point in a more general way, let us revisit energy conservation while including the possibility that the particle number is allowed to change. For this, let us define a new quantity, called **the chemical potential**. *The chemical potential is the energy cost of adding a particle to the system while no heat exchange takes place and no mechanical work is done:* $\mu \equiv [E(N+1) - E(N)]_{S,V}$. Since $E(N+1) - E(N) = \frac{E(N+1) - E(N)}{1} = \frac{E(N+1) - E(N)}{(N+1) - N}$ and $N \gg 1$, this can be re-written as the following derivative:

$$(18) \quad \mu \equiv \left(\frac{\partial E}{\partial N} \right)_{S,V}$$

We can now write the energy conservation for systems with a variable particle number:

$$(19) \quad dE = TdS - pdV + \mu dN$$

or, equivalently,

$$(20) \quad \begin{aligned} T &= \left(\frac{\partial E}{\partial S} \right)_{V,N} \\ -p &= \left(\frac{\partial E}{\partial V} \right)_{S,N} \\ \mu &= \left(\frac{\partial E}{\partial N} \right)_{S,V} \end{aligned}$$

Note that at this point, we are still considering pure systems, i.e., those containing just one chemical species. Mixtures will be considered in due time.

Thus for the increment of the Gibbs free energy we obtain

$$(21) \quad dG = d(E - TS + pV) = dE - d(TS) + d(pV) = dE - (TdS + SdT) + (pdV + Vdp)$$

which leads, in view of Eq. 19, to

$$(22) \quad dG = -SdT + Vdp + \mu dN$$

or, equivalently,

$$\begin{aligned}
-S &= \left(\frac{\partial G}{\partial T} \right)_{p,N} \\
V &= \left(\frac{\partial G}{\partial p} \right)_{T,N} \\
\mu &= \left(\frac{\partial G}{\partial N} \right)_{T,p}
\end{aligned}
\tag{23}$$

Likewise, the increment of the Helmholtz energy, $A = E - TS$, for a system with a variable particle number becomes

$$(24) \quad dA = -SdT - p dV + \mu dN$$

or, equivalently,

$$\begin{aligned}
-S &= \left(\frac{\partial A}{\partial T} \right)_{V,N} \\
-p &= \left(\frac{\partial A}{\partial V} \right)_{T,N} \\
\mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V}
\end{aligned}
\tag{25}$$

And, finally we introduce a new function, called the **enthalpy**, or the **heat function**:

$$(26) \quad H = E + pV$$

Since $dH = d(E + pV) = dE + p dV + V dp$, one obtains

$$(27) \quad dH = T dS + V dp + \mu dN$$

or, equivalently,

$$\begin{aligned}
T &= \left(\frac{\partial H}{\partial S} \right)_{p,N} \\
V &= \left(\frac{\partial H}{\partial p} \right)_{S,N} \\
\mu &= \left(\frac{\partial H}{\partial N} \right)_{S,p}
\end{aligned}
\tag{28}$$

The increments of all four energy functions given above display a clear pattern: They all have simple-looking derivatives for certain choices of independent parameters, as summarized in the Table below:

$E = E(S, V, N)$	$dE = TdS - p dV + \mu dN$
$A = A(T, V, N)$	$dA = -SdT - p dV + \mu dN$
$G = G(T, p, N)$	$dG = -SdT + V dp + \mu dN$
$H = H(S, p, N)$	$dH = TdS + V dp + \mu dN$

Other choices of variables are possible so long as

1. The number of the variables is exactly three.
2. At least one of those three variables corresponds to an extensive quantity. This is needed because each one of the four energies is an extensive quantity itself and so at least one of the variables must contain information as to the size of the system.

The converse of the item 2 is worth elaborating on: If expressed per particle, each of the four energies no longer depends on N and, thus, is a function of exactly *two* variables. Both of these remaining variables cannot contain information about the system size and, thus, must be intensive. Now let us take every item in the 1st column of the table above and re-write it *per particle*. In those cases where one or both of the arguments are extensive variables, we must replace them with their intensive counterparts per particle:

$$\begin{aligned}
 \frac{E}{N} &= \epsilon \left(\frac{S}{N}, \frac{V}{N} \right) \\
 \frac{A}{N} &= a \left(T, \frac{V}{N} \right) \\
 \frac{G}{N} &= g(T, p) \\
 \frac{H}{N} &= h \left(\frac{S}{N}, p \right)
 \end{aligned}
 \tag{29}$$

One immediately notices that of the four energies, the Gibbs energy has the simplest N dependence:

$$(30) \quad G = N g(p, T)$$

and so

$$(31) \quad \left(\frac{\partial G}{\partial N} \right)_{T,p} = g(p, T)$$

comparing this result with the bottom equation from Eq. 23, one immediately obtains $\mu = g(p, T)$. In view of Eq. 30 this lead to the remarkable result that the chemical potential is, in fact, the Gibbs free energy per particle!

$$(32) \quad G = N \mu$$

It is also clear from the above discussion that only two intensive variables are independent, while any other intensive property can be expressed as their function. A useful instance of such a functional relation can be obtained by noticing that $dG = d(N\mu) = Nd\mu + \mu dN$ and subtracting $dG = Nd\mu + \mu dN$ from Eq. 22. This yields what is known as the Gibbs-Duhem equation:

$$(33) \quad N d\mu = -SdT + V dp$$

It becomes particularly lucid when written out in terms of quantities per particle, which is accomplished by dividing it by the particle number:

$$(34) \quad d\mu = -s dT + v dp$$

where $s \equiv S/N$ is the specific entropy and $v \equiv V/N$ specific volume. Every quantity in the above equation is intensive. Thus we obtain $s = -(\partial\mu/\partial T)_p$ etc., as just advertised.

Why do we call enthalpy the “heat function”? Because it directly reflects the amount of exchanged heat during an isobaric process. (“Isobaric” means “at constant pressure”.) Indeed, per Eq. [27](#),

$$(35) \quad (dH)_{p,N} = T dS$$

If, in addition, the temperature is kept constant as well, one can easily integrate this to obtain

$$(36) \quad (\Delta H)_{p,T,N} = T (\Delta S)_{p,T,N}$$

(Clearly, the system must change its volume during such a process!)

Another consequence of Eq. [35](#) is a useful expression for the heat capacity at constant pressure:

$$(37) \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

This indicates that the enthalpy is essentially the constant-pressure analog of the energy.

Finally, one may also write down simple relations between the thermodynamic functions, such as

$$(38) \quad G = A + pV$$

or

$$(39) \quad G = H - ST$$

As an illustration of the utility of these and earlier expressions, let us determine the expression for the chemical potential of a single-component ideal gas. First re-write Eq. [19](#) as

$$(40) \quad dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

and so

$$(41) \quad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{E,V}$$

To use this formula, we must express the entropy as a function of the three variables E , V , and N exclusively. (This means that any other quantity that could be involved in the available expression must be expressed through those three variables.) Just such an expression is available in Eq. [6](#). Differentiating it w.r.t. N , while keeping E and V fixed, yields:

$$(42) \quad \begin{aligned} -\frac{\mu}{T} &= c_V \left[\ln \left(\frac{E}{N c_V T^\ominus} \right) - 1 \right] + k_B \ln \left(\frac{V}{V^\ominus} \right) \\ &= k_B \ln \left[\left(\frac{E}{e N c_V T^\ominus} \right)^{c_V/k_B} \left(\frac{V}{V^\ominus} \right) \right] \end{aligned}$$

Here we use that $\ln x - 1 = \ln(x/e)$, where $e \equiv \exp(1)$, and $y \ln x = \ln(x^y)$. Substituting $E = N c_V T$, one obtains a compact expression:

$$(43) \quad \mu = -k_B T \ln \left[\left(\frac{T}{e T^\ominus} \right)^{c_V/k_B} \left(\frac{V}{V^\ominus} \right) \right]$$

which, again, emphasizes the role of $k_B T$ as the basic thermal energy scale for a particle, but modified to

account for specific conditions. The above expression can be re-written for other combinations of parameters, using the equation of state. It can be also used to write down expressions for the thermodynamic functions. And so, for instance, for a process conserving the particle number, one gets

$$(44) \quad G - G^{\ominus} \equiv \Delta G = N \Delta \mu$$

The corresponding Helmholtz free energy is, by virtue of Eq. [38](#):

$$(45) \quad \Delta A = \Delta G - \Delta(pV)$$

8.

Phase Transitions

We have so far dealt largely with systems whose free energy has just one minimum. Changing the volume and/or energy of a system with just one minimum is much like compressing/stretching a mechanical spring. The length and the tension of the spring may change in the process, yet microscopically, the material is much the same as in the absence of external load and will return back to its initial state once the load is off. Consistent with this notion, a thermodynamic state corresponds to a vast set of rather similar microstates that are explored as the system fluctuates. These fluctuations are thus intrinsic physically but are also inherent to the very definition of a thermodynamic state. One should not be misled by the fact that the fluctuations of extensive variables are relatively small, for large systems. In reality, *local* fluctuations of extensive variables such as the energy, volume, etc., are substantial but largely cancel out when added together. For instance, the average of the total energy of a system of size N scales proportionally with N , while the fluctuation of the total energy goes only as \sqrt{N} , a much slower function of N . Nonwithstanding these fluctuations, the system characterized by a single minimum has only one thermodynamic state, or “phase”, to speak of.

Let us now consider an alternative situation where the pertinent thermodynamic potential has *two* minima. It will be most practical to consider a reduced form of the thermodynamic potential \tilde{G} from the preceding Chapter, where we leave the volume V as a variable while setting the energy at its likeliest value for each individual value of volume V :

$$(1) \quad \tilde{G} \equiv E_{\text{mp}}(T, V, N) - TS[E_{\text{mp}}(T, V, N), V, N] + pV$$

Physically, this corresponds to a situation where we have thermal equilibrium in place but not the mechanical equilibrium, unless it so happens that the current value V is at the stable minimum of \tilde{G} . Next, we recognize that the first two terms on the r.h.s. of Eq. 1 actually correspond to the equilibrium value of the Helmholtz free energy $A = E_{\text{mp}} - TS(E_{\text{mp}}, V)$, and so

$$(2) \quad \tilde{G} \equiv A(V, T, N) + pV$$

In *full* equilibrium, not just thermal equilibrium, the system must reside in the lowest minimum of this function with respect to the variable V . Indeed, optimizing w.r.t. to V leads to an equation we had derived earlier through a somewhat different route:

$$(3) \quad \frac{\partial}{\partial V}(A + pV) = 0 \Rightarrow \left(\frac{\partial A}{\partial V} \right)_{T, N} = -p$$

We reiterate that in the l.h.s. formula, the pressure p is regarded as fixed by bringing our system in mechanical contact with an environment maintained at pressure p .

The above equation gives a necessary condition for the function to have an extremum. In addition, we must stipulate that the extremum actually be a *minimum*, so that the equilibrium is stable. The l.h.s. panel in the figure below illustrates that in this case, fluctuations that cause the volume to decrease subsequently lead to an increase in the pressure of the system: $\frac{\partial}{\partial V}(A + p_0 V) = -p + p_0 < 0 \Rightarrow p > p_0$, where we denoted the pressure in the environment with p_0 to distinguish it from the system's pressure $p = -(\partial A / \partial V)_T$, which is equal to p_0 only in equilibrium, see Eq. 3. This excess pressure, then, drives the system back to the equilibrium value of the volume, i.e., until $p = p_0$. Likewise, there is a restoring force toward equilibrium for fluctuations that cause the volume to increase:

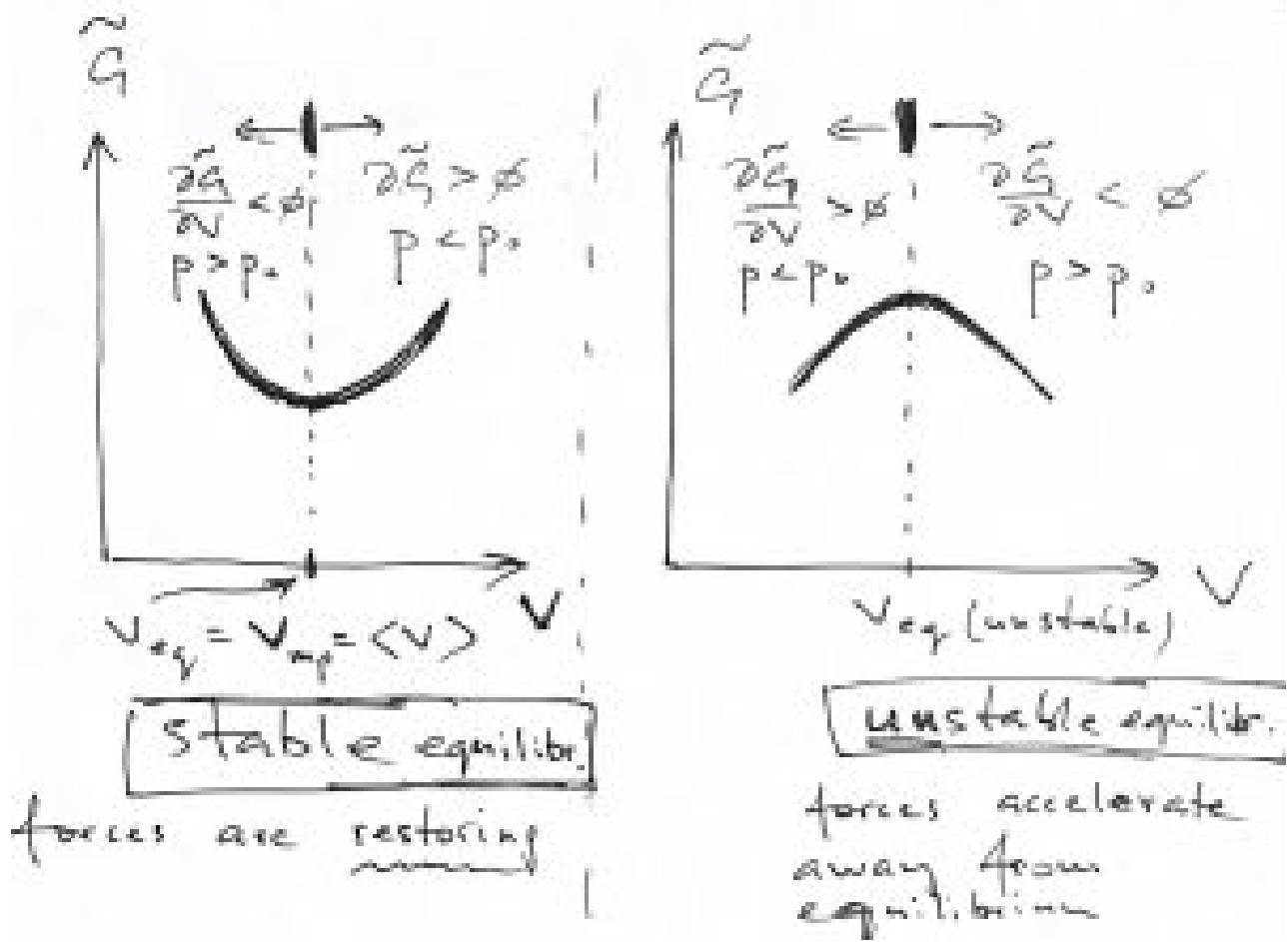


Figure 1

Conversely, an unstable minimum implies that if the system wanders off the equilibrium, it will precipitously continue moving away from the equilibrium, as the r.h.s. panel in the above Figure demonstrates. Indeed, if the volume is less than its value at the maximum, the pressure in the system decreases thus allowing the external pressure to compress the system even further and so on.

In order for the extremum to actually be a minimum, we must require that the second derivative be positive, which, then, implies that the second derivative of the Helmholtz free energy w.r.t. the volume should be positive, too, since the two functions differ only by a linear function of volume, $p\tilde{V}$, whose 2nd derivative vanishes:

$$(4) \quad \left(\frac{\partial^2 \tilde{G}}{\partial V^2} \right)_{p,T} > 0 \Rightarrow \left(\frac{\partial^2 A}{\partial V^2} \right)_T > 0$$

We can use Eq. 3 to further simplify this condition:

$$(5) \quad \left(\frac{\partial^2 A}{\partial V^2} \right)_T = \left(\frac{\partial(\partial A / \partial V)_T}{\partial V} \right)_T = - \left(\frac{\partial p}{\partial V} \right)_T > 0$$

Comparing this inequality with the definition of the isothermal compressibility, we conclude the system is mechanically stable, if its isothermal compressibility is positive:

$$(6) \quad \kappa_T > 0$$

which is completely analogous to the earlier established notion that the heat capacity must be positive for the system to be stable w.r.t. thermal fluctuations.

Thus, according to the condition 4, the system is stable if the Helmholtz free energy, as a function of V ,

is concave up throughout. This insures that the function \tilde{G} has only one minimum and that there is only one thermodynamic states to speak of, as we discussed in the beginning.

Conversely, if $A(V)$ has a *convex-up* portion, we expect that a certain subset of microstates become inaccessible, since they correspond to mechanically unstable configurations:

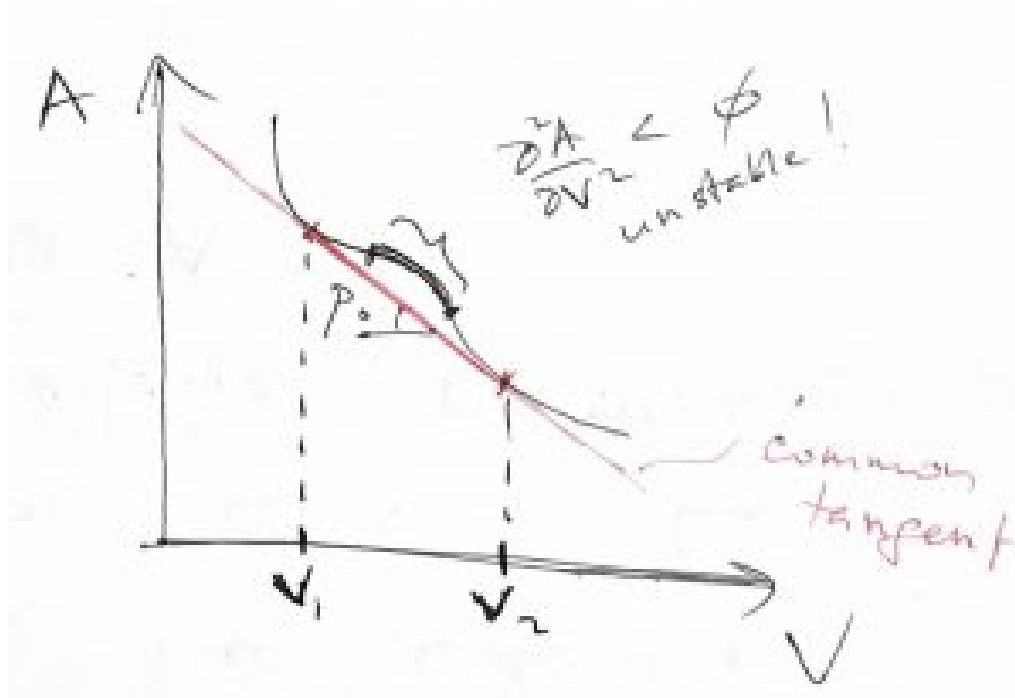


Figure 2

Here and until further notice, we will be working at constant temperature:

(7) $T = \text{const}$

The region of negative curvature in the above figure separates two regions of positive curvature. In other words, the set of inaccessible configurations in the Figure above—i.e. the $(\partial^2 A / \partial V^2)_T < 0$ portion—separate two sets of physically realizable configurations—i.e. the two $(\partial^2 A / \partial V^2)_T > 0$ portions—each set corresponding to a thermodynamic state. These two accessible thermodynamic states are distinct in this formal sense and, generally, exhibit distinct physical properties as well, as we will observe later. As such, we regard such distinct thermodynamic states are distinct **phases**. If the common tangent to the $A(V)$ curve above has the slope $(-p_0)$, we can readily convince ourselves that one can drive the system to the low volume phase (phase 1) by applying external pressure in excess of p_0 and vice versa for the high volume phase:

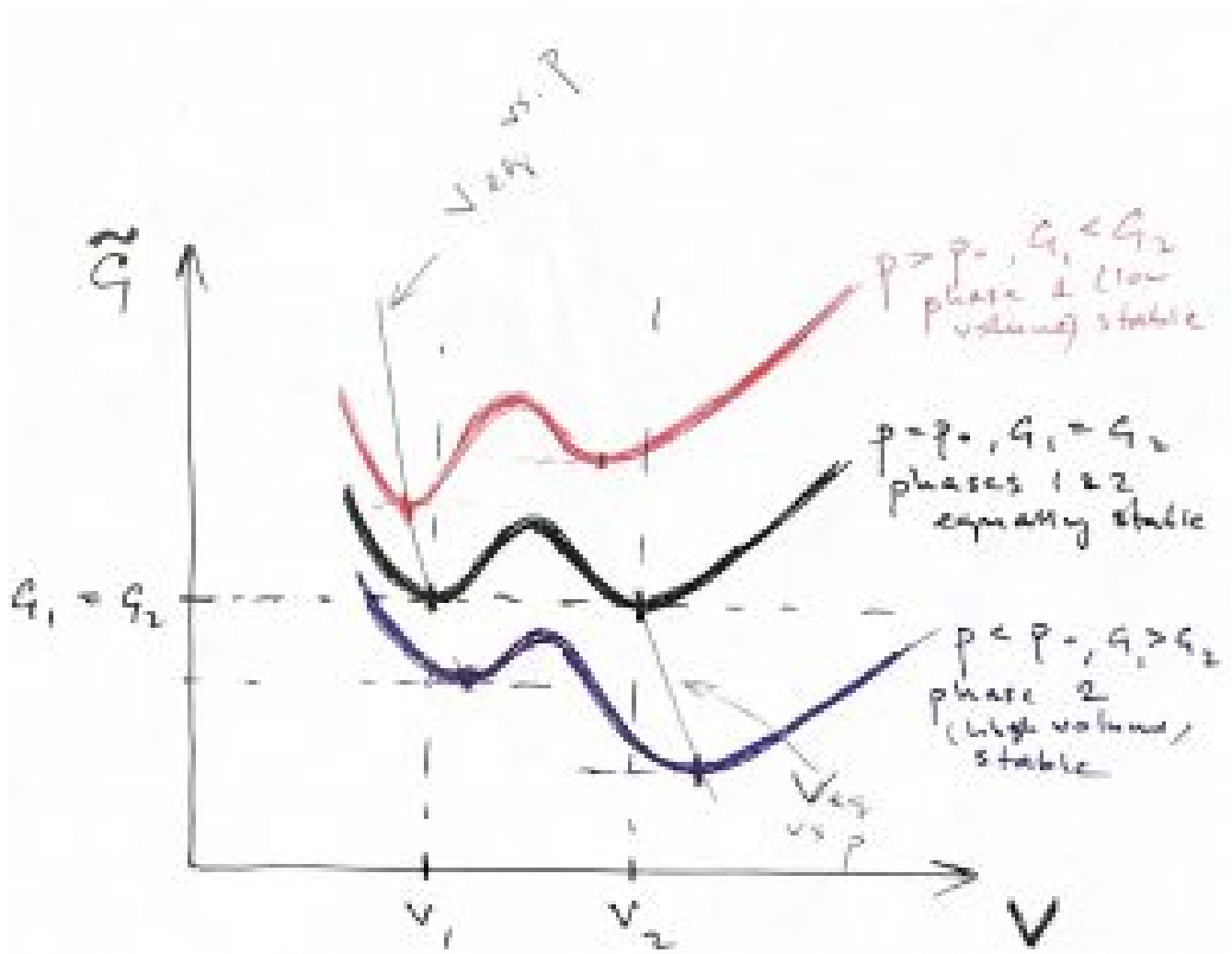


Figure 3

According to the Figure above, if one maintains a fixed pressure $p < p_0$, the system will spontaneously relax to the high-volume phase while for $p > p_0$, the system will spontaneously relax to the low-volume phase. Only when $p = p_0$ do the two phases become equally stable, and so the system will relax to one or the other state depending on which side of the col separating the two minima it is prepared. It is instructive to graph the resulting pressure dependence of the *equilibrium* volume:

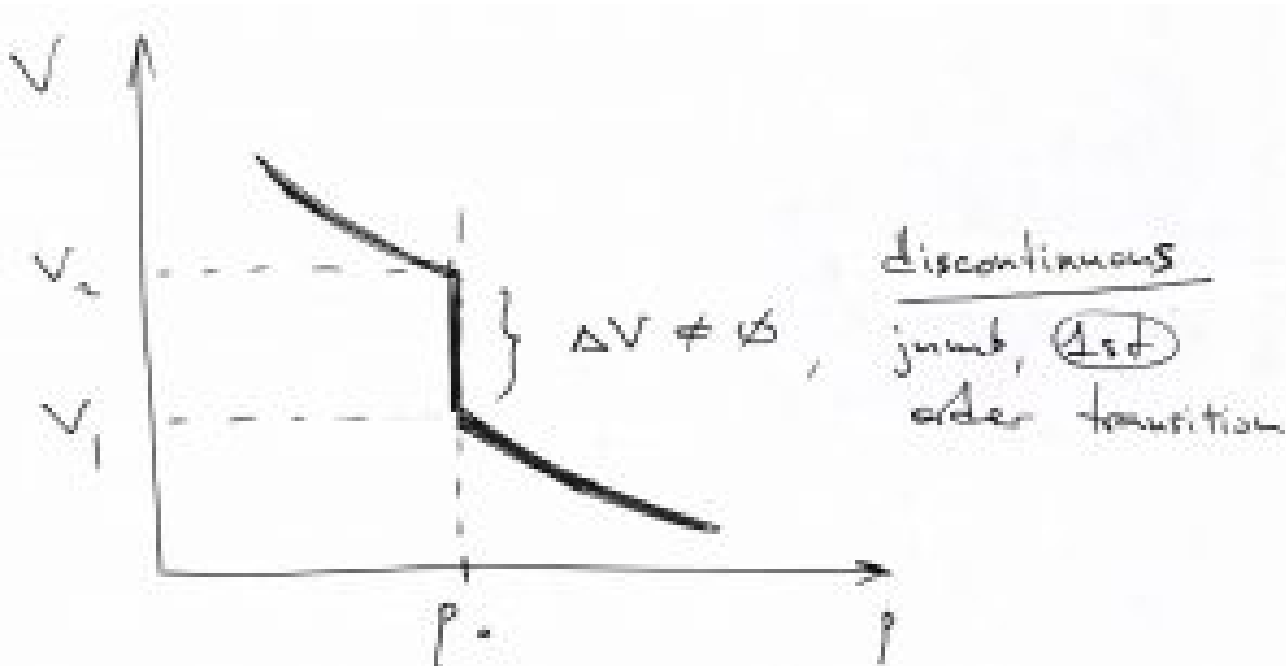


Figure 4

This is a remarkable result! The volume exhibits a discontinuous jump at a particular value of pressure. We call such remarkable situations **phase transitions**. Specifically, when the relevant control parameter experiences a discrete jump like the one above, we call such transitions discontinuous. A common, though dated, term for such discontinuous phase transitions is the 1st order transition, the word “1st order” referring to the fact the 1st derivative of the free energy w.r.t. to the driving force of the transition (pressure in this case), exhibits a discontinuity.

Since the minimum value of the \tilde{G} function is the equilibrium value of the Gibbs free energy, we conclude that the Gibbs free energies of phase 1 and phase 2 are mutually equal when the two phases are in equilibrium, since the corresponding two minima are exactly of the same depth at the transition:

$$(8) \quad G_1 = G_2 \text{ or } \Delta G = 0$$

In view of $G = \mu N$, this implies that the chemical potentials of the two phases are, in fact, equal as well:

$$(9) \quad \mu_1 = \mu_2$$

We reiterate that the above equation embodies the condition that the two phases are in equilibrium w.r.t. particle exchange. (If one phase is more stable than the other, then the stable phase has a lower chemical potential, as should be clear from the Figure above.) The condition in Eq. 9 supplements the other two equilibrium conditions that we had imposed by construction:

$$T_1 = T_2$$

$$(10) \quad p_1 = p_2$$

the first one taking care of thermal equilibrium and the second one of mechanical equilibrium.

In many cases and, specifically for the vapor—liquid transition, we control not the pressure but the *total* volume of the system. In this case, the system cannot convert between the phases all at the same time if the total volume is made to change *continuously*. Instead, the system will convert locally, so that the new phase occupies a progressively larger portion of the space. And so the continuity of the total volume, despite the discontinuity in the volumes of the individual phases, is realized through the continuity of the mole fractions of the two phases. We illustrate this state of affairs using the vapor—liquid transition as an example:

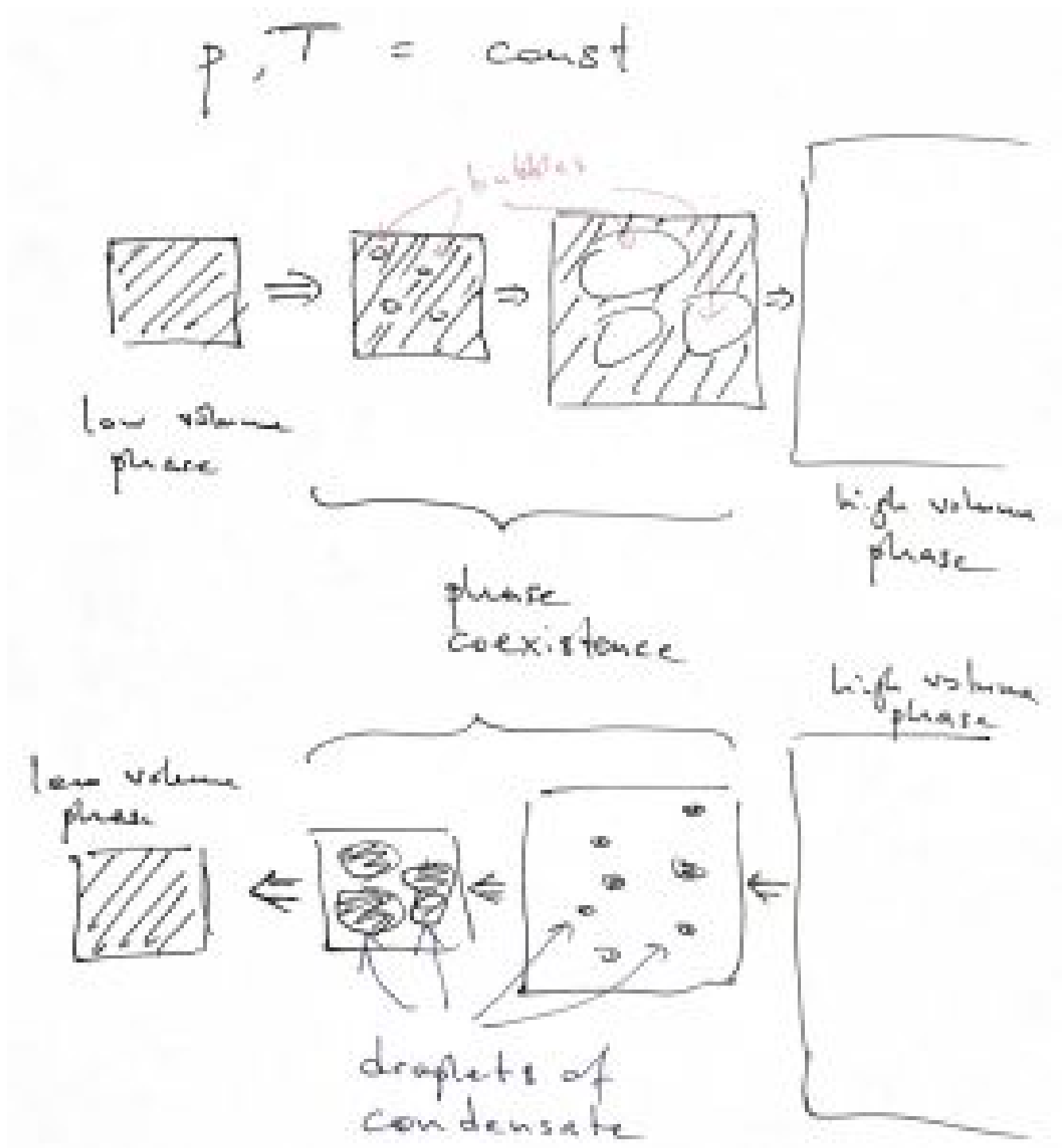


Figure 5

Suppose that during such **phase coexistence** (during which the two phases literally spatially coexist in one volume) the mole fraction of phase 1 is x_1 and the mole fraction of phase 2 is x_2 . ($x_1 + x_2 = 1$, of course.) Then, the total volume of the system is just the volume that the system would have if it were in pure phase 1, times the mole fraction of phase 1, plus the same thing for phase 2:

$$(11) \quad V = x_1 V_1 + x_2 V_2 = x_1 V_1 + (1 - x_1) V_2$$

Here we ignore the volume of the interface spatially separating the two phases. The interface width is usually

very small, in which case the volume of such and interfacial region is much smaller than the volume of either of the pure phases. By the same token, the total free energy is

$$(12) \quad A = x_1 A_1 + (1 - x_1) A_2$$

Eliminating x_1 from the two equations above yields that for a phase separated system—which is the equilibrium configuration for $V_1 < V < V_2$ —the free energy depends linearly on the total volume V :

$$(13) \quad A = \frac{V_2 - V}{V_2 - V_1} A_1 + \frac{V - V_1}{V_2 - V_1} A_2$$

We show this in the Figure below. Consistent with the 2nd Law, the equilibrium value of the free energy (solid black line) is less than the non-equilibrium value (red line), which the system would have if it remained spatially homogeneous:

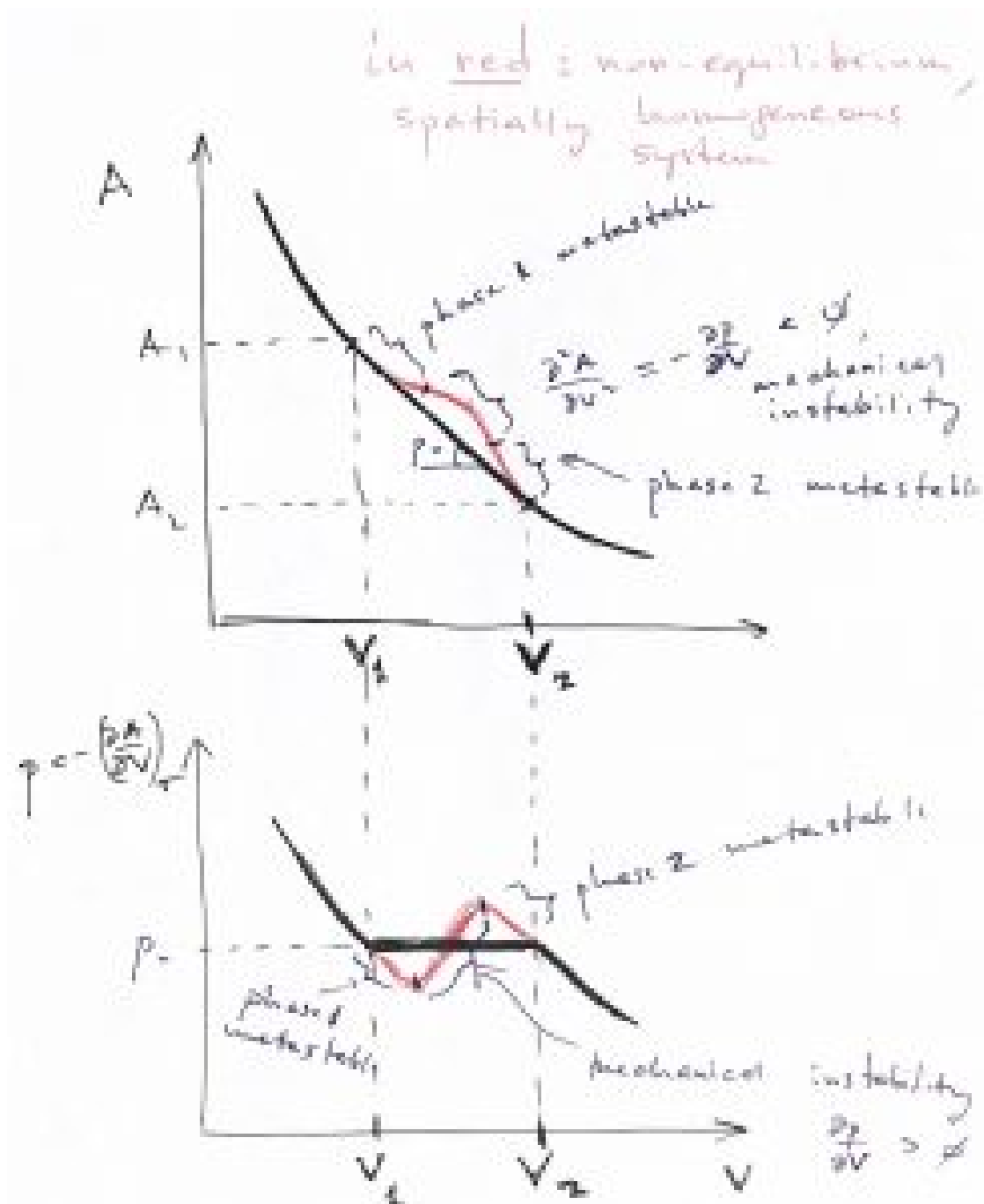


Figure 6

Alongside we also showed the corresponding dependence of the pressure on the volume, again at constant temperature. Such curves are called *isotherms*. One should recognize that the isotherm shown above is the same as the V vs. p curve shown earlier, but the graph is now “flipped” so that V is now the horizontal axis and p is the vertical axis.

The equilibrium isotherm directly shows that once phase separation begins, the systems remains at constant pressure and temperature until it is fully converted to the other phase. We note that in order for a clean liquid to *begin* to develop bubbles, it must be somewhat over-dilated and/or over-heated. In other words, one must decrease the pressure somewhat below the pressure p_0 and/or heat the liquid somewhat above the equilibrium boiling temperature. Likewise, in order for the vapor to *begin* condensing, it must be somewhat cooled below the equilibrium boiling temperature and/or somewhat compressed beyond the pressure at which the vapor and

liquid would co-exist at the temperature in question. This is because of the interfacial regions we mentioned in passing earlier. In the very beginning of the phase-to-phase conversion, the amount of interfacial matter relative to the amount of the new (“minority”) phase is actually not small. At the same time, there is a free energy cost associated with the system being uniform at volume V such that $V_1 < V < V_2$, per Fig. 6. (The free energy of the spatially-uniform, non-equilibrium branch is higher than that of the equilibrium, phase-separated branch.) As a result, some extra stabilization of the minority phase is needed to compensate for the free energy cost of creating the interface. In practice, nucleation of the minority phase is often facilitated by impurities, dirt, and roughness of the container walls, etc.

The vapor-liquid transition is special in that the volume discontinuity tends to decrease with the temperature of the transition and, in fact, vanishes at the so called *critical point*. We illustrate this below using isotherms for three select values of the temperature: below, at, and above the critical temperature:

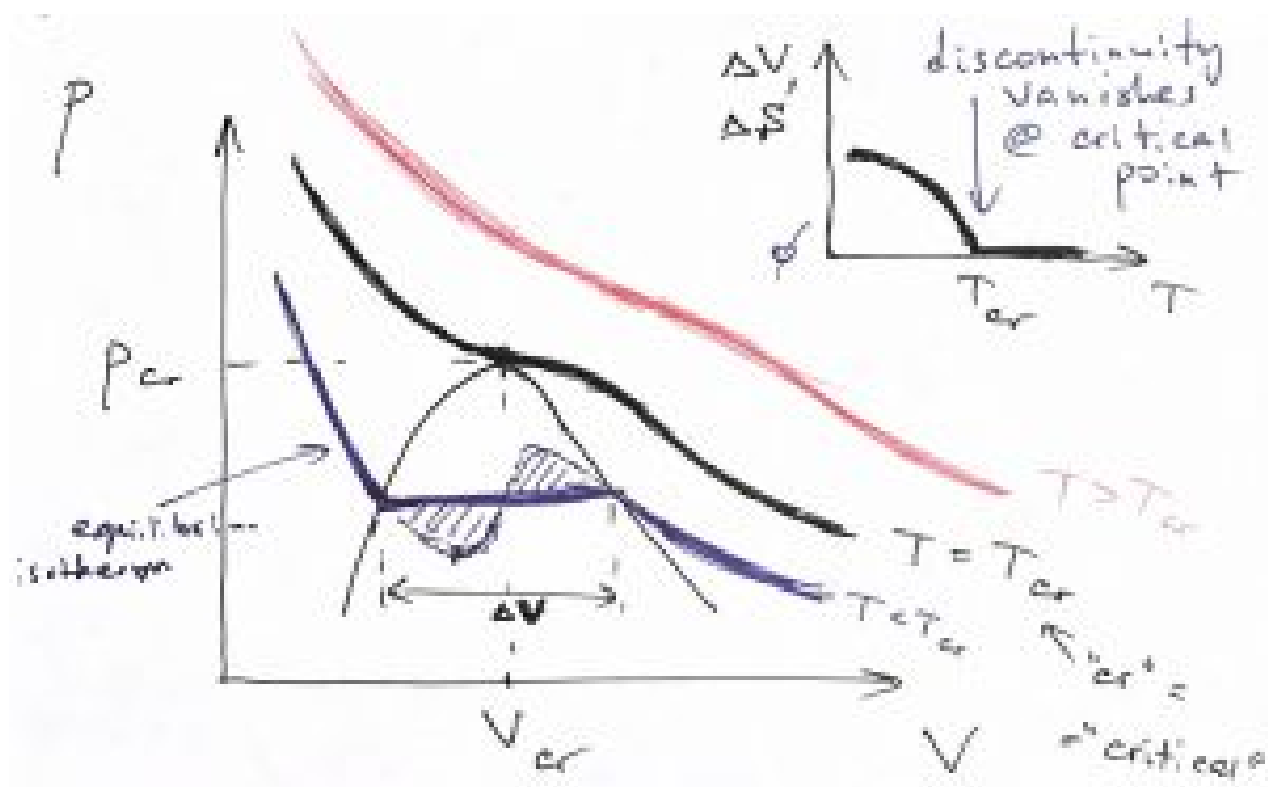
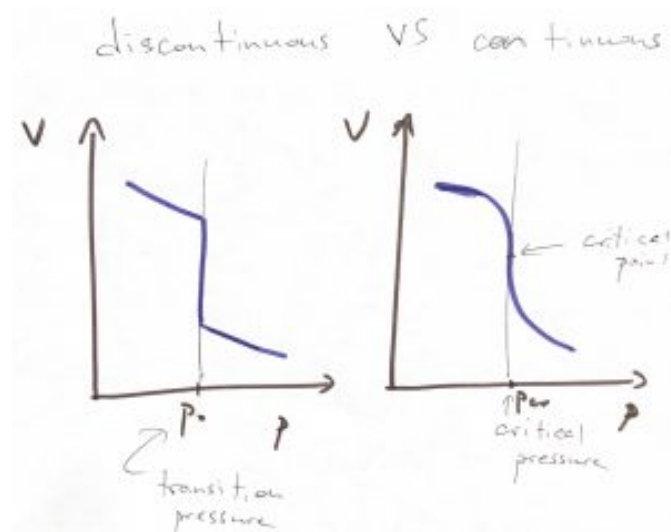
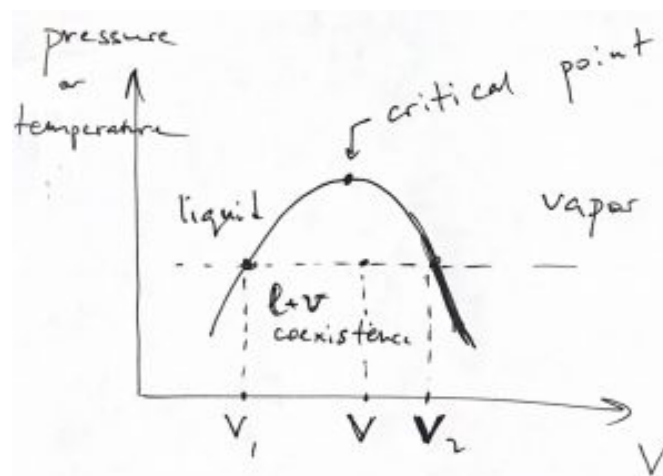


Figure 7

At the critical point, the pressure dependence of the volume still has a divergent derivative but, nonetheless, remains continuous:



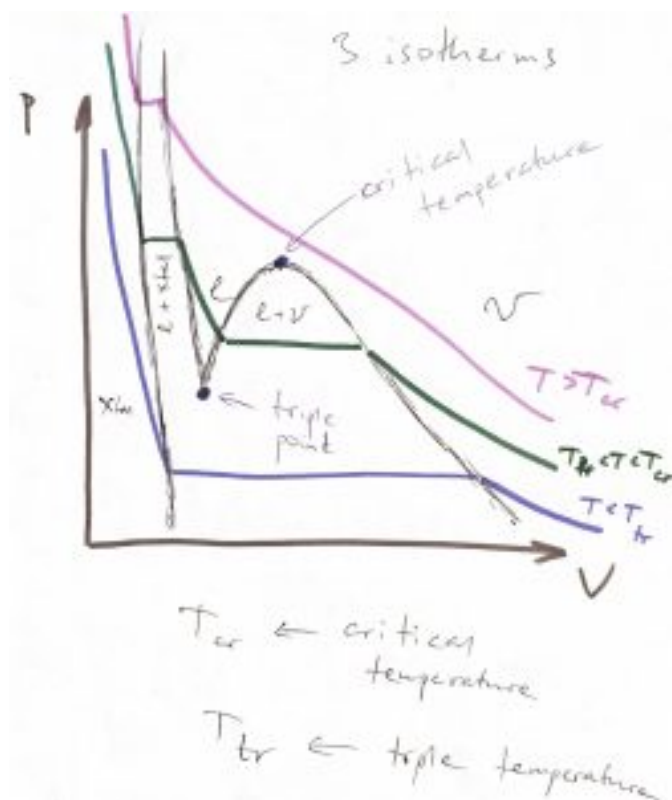
As illustrated in Fig.7, to each temperature there corresponds a unique value of pressure at which vapor-liquid coexistence will be observed. (This pressure grows monotonically with temperature, as we will see shortly.) Thus, one could similarly draw a set of isobars, as see also below. In either case, it is instructive to show the volumes of the pure phases in one graph for a range of temperature or pressure, as we illustrate below:



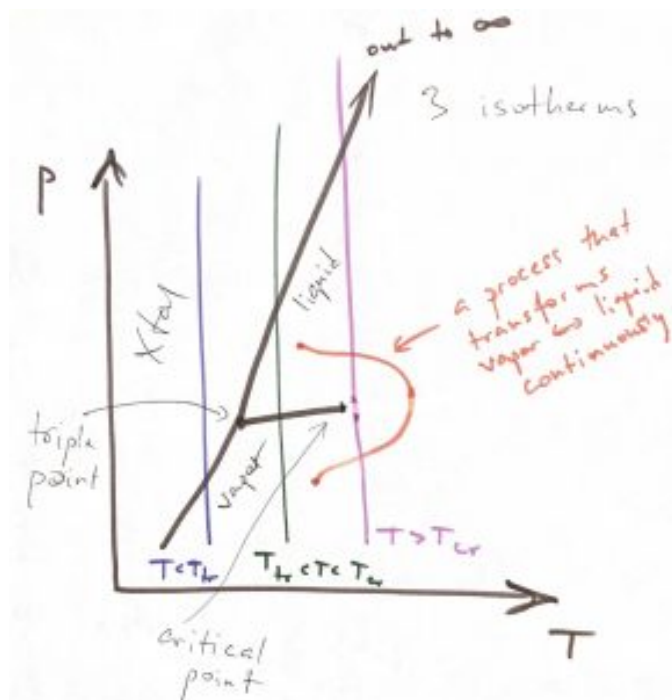
The volumes V_1 and V_2 depend on the pressure (temperature). There is one-to-one correspondence between the total volume of a phase-separated system and the mole fraction of the two phases, as we have already seen in Eq. [11](#). We re-write this equation in a slightly different form, which is known as the **lever rule**:

$$(14) \quad \frac{x_2}{x_1} = \frac{V - V_1}{V_2 - V}$$

Now, what happens to the liquid or gas if one continues to lower temperature and/or pressure? A common scenario is that both will eventually convert into a crystalline solid, as we illustrate in the figure below, where we show three kinds of coexistences in one diagram: liquid-Xtal, liquid-vapor, and Xtal-vapor:

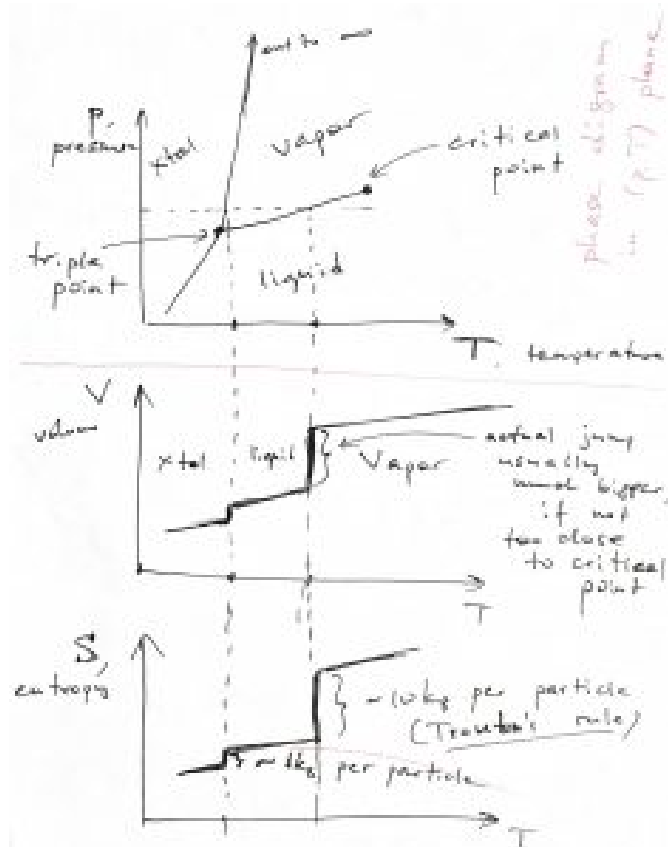


The three isotherms in the figure above can also be shown on a $p - T$ phase diagram, where they become straight lines, as below:



As a bonus feature, we showed above a process, using an orange curve, that takes one between the vapor and liquid state without crossing the phase boundary. This is a unique consequence of the liquid-vapor transition where the phase boundary ends at a finite temperature—thus resulting in a critical point—and signifying that the vapor and liquid are fundamentally equivalent phases. Namely, these are phases where the particles are allowed to freely translate on the experimental time scale.

Just as well, one can perform constant pressure experiments:



We see that for sufficiently low pressures a gas can turn into a solid bypassing the liquid state. The volume changes for the gas-crystal and gas-liquid transitions can be arbitrarily large. (The volume change for the gas-liquid transition *can* be small, but this is seen only close enough to the critical point.) In contrast, the entropy changes for such transitions seem vary less from substance to substance. And so, for instance the entropy change for the liquid-to-vapor transition is numerically close to $10 k_B$ per particle:

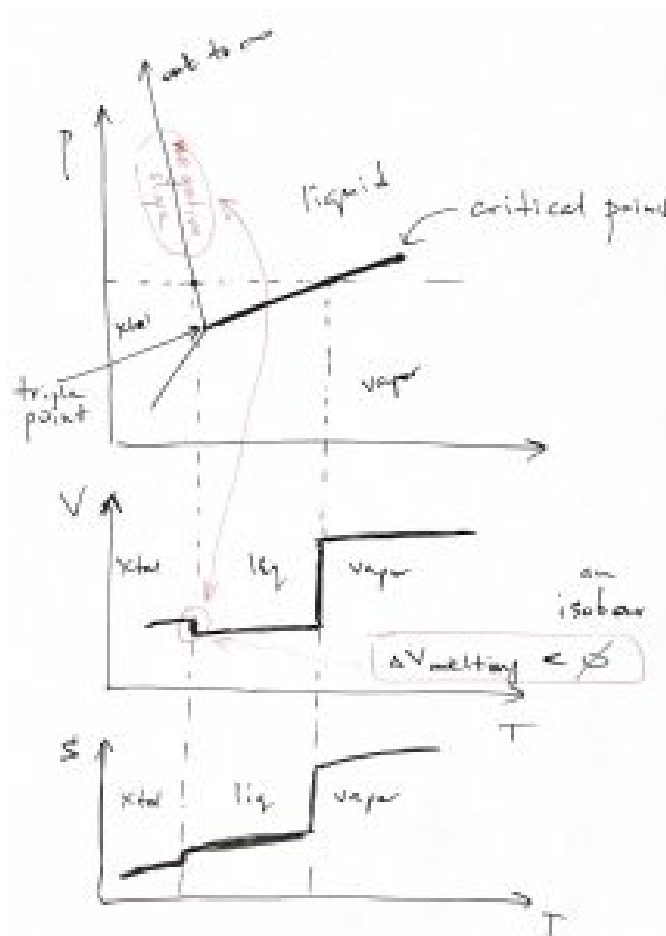
$$(15) \quad \Delta s_{\text{evaporation}} \simeq 10 k_B$$

which is known as **Trouton's Rule**. Trouton's rule does break down close to the critical point, where the entropy change must vanish, see also below.

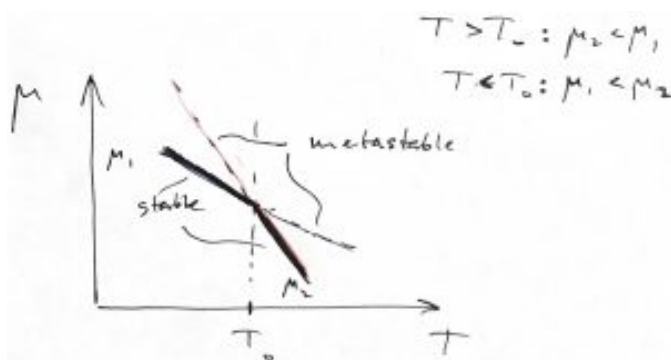
The entropy of melting is also quite consistent among different substances and is always on the order of $1 k_B$ per particle, usually numerically close to $1.5 k_B$, but could be larger for large molecules:

$$(16) \quad \Delta s_{\text{melting}} \simeq 10^0 k_B$$

A number of substances, some of which are extraordinarily important, exhibit the interesting property that their volume actually *decreases* when they melt, while the corresponding phase boundary on the (p, T) has a negative slope. These important substances include water and elemental silicon and germanium.



At the same time, the entropy always increases during a transition driven by heating the system. We can use Thermodynamics to understand this. First, let us sketch the Gibbs free free energy per particle, i.e. the chemical potential, for both phases as functions of temperature:



The stable phase is the one with the lower value of μ , and so according to the above Figure, phase 1 is the low temperature phase and phase 2 is the high-temperature phase. For geometrical reasons, the (negative) slope of the $\mu_2(T)$ dependence should be greater than the (negative) slope of the $\mu_1(T)$ dependence, as the picture above demonstrates. And so,

$$(17) \quad - \left(\frac{\partial \mu_2}{\partial T} \right)_p \Big|_{T=T_0} > - \left(\frac{\partial \mu_1}{\partial T} \right)_p \Big|_{T=T_0}$$

But according to the Gibbs-Duhem equation, $d\mu = -sdT + vdp$, we have $-(\partial\mu/\partial T)_p = s$, i.e., the

entropy per particle. Thus we obtain that the entropy always *increases* for a transition from a low-temperature phase to a high-temperature phase: $s_2(T_0) > s_1(T_0)$, or,

$$(18) \quad \Delta S > 0 \text{ for low-}T \text{ to high-}T \text{ phase transition}$$

This is natural. Indeed, as one increases the temperature or, at least, attempts to increase the temperature, one must put heat *into* the system. In fact, we can use Eq. 8, $0 = \Delta G = \Delta(H - TS) = \Delta H - T\Delta S$, to show that the enthalpy of the transition is simply the entropy of the transition times the temperature:

$$(19) \quad \Delta H = T\Delta S$$

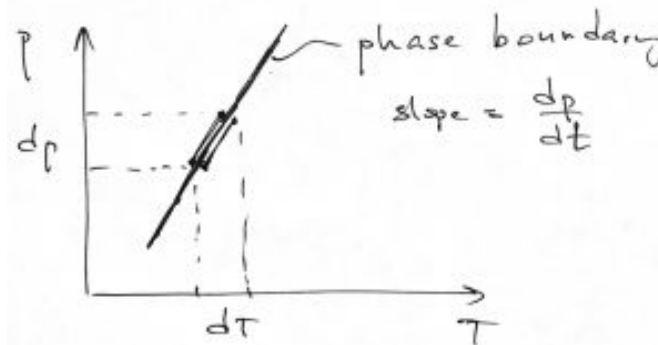
which, again, is always positive for a transition driven by *heating*. We note that the temperature staying constant during the phase transformation is an example of the *Le Chatelier principle*, which states that the system will respond to an external perturbation so as to minimize the effect of the perturbation. Indeed, the absorbed heat goes toward phase transformation, as if the system resisted to our attempts to increase its temperature.

Note that the converse is also true: During a transition from the higher-temperature to the low-temperature phase, heat will be *released*.

Because the temperature stays constant during phase transformations, one defines the specific heat of the transition per some unit of the substance such as mass or mole.

Transitions driven by changing the pressure have an analogous property: The high pressure phase will always have a lower volume than the low pressure phase. Indeed, according to the Gibbs-Duhem equation, $(\partial\mu/\partial p)_T = v$, v being the specific volume. This is, again, an instance of the Le Chatelier principle. Note that because the volume of water is lower than that of ice, one can actually induce melting by compressing ice. And incredibly important consequence of the fact that ice is lighter than water is that the bottom of the ocean does not solidify despite the humongous pressure due to the water mass above it. This allows for a great thickness of the ocean and was, likely, essential for the preponderance of early water organisms that produced oxygen, which, then, allowed for more complex life forms. For the same reason, fresh water lakes and rivers freeze near the surface—the ice does not sink because it is lighter—and so deep lakes and rivers do not freeze through during the winter. This allows complex organisms living in those reservoirs and whose life cycles exceed one year to survive the winter.

Now in contrast with entropy, the *volume* change during a transition caused by heating or cooling could be of either sign, as we have already seen. Microscopically, this can be caused by a variety of reasons. For instance, water ice or crystalline silicon are characterized by highly directional bonding resulting in rather open structures. When these open structures melt, the bonds partially break causing the coordination number to actually increase, which, then, causes a decrease in volume. Let us show that the sign of the volume change determines the slope of the corresponding phase boundary on the pressure-temperature plane. Indeed, consider a small increment of the temperature while moving along one side of the boundary and along the other side of the boundary, respectively:



For these two processes, we can write the Gibbs-Duhem equation for the corresponding increment in the chemical potential:

$$d\mu_1 = -s_1 dT + v_1 dp$$

$$(20) \quad d\mu_2 = -s_2 dT + v_2 dp$$

where indices 1 and 2 refer to the two sides of the phase boundary. Next we note that the chemical potentials on

the opposite sides of the phase boundary are always mutually equal. This implies that $d\mu_1 = d\mu_2$. Subtracting the two equations above from each other gives the following simple expression for the slope of the phase boundary:

$$(21) \quad \frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

where Δs and Δv are the entropy and volume changes for the transition at the pressure and temperature in question. One must be consistent in computing these changes. For instance, if $\Delta s = s_2 - s_1$, then $\Delta v = v_2 - v_1$. Conversely, if $\Delta s = s_1 - s_2$, then $\Delta v = v_1 - v_2$.

The above equation is known as **the Clausius-Clapeyron equation**. It can be written in a variety of forms. For instance, one can use Eq. 19 to write it as

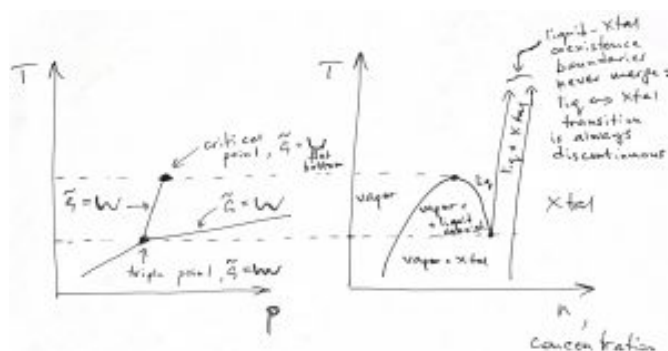
$$(22) \quad \frac{dp}{dT} = \frac{\Delta h}{T\Delta v}$$

where Δh is the enthalpy of the transition per particle. Note that because both the enthalpy and volume are extensive variables, we can re-write the r.h.s. in a variety of ways while being mindful that both the enthalpy and volume must be given per the same unit of matter, be it a mole or kilogram, or whatnot.

According to Eq. 21, for transitions that are driven by heating, $\Delta s > 0$, but exhibit a negative volume change, $\Delta v < 0$, the slope dp/dT must be negative, as is the case experimentally.

Eq. 21 also helps understand why the slope of the liquid-Xtal boundary is steeper than the slope of the liquid-vapor boundary. Indeed, despite the greater value of $\Delta s_{\text{vaporization}}$, relative to $\Delta s_{\text{melting}}$, the volume changes accompanying vaporization are even greater. Recall that the specific volume of a gas at normal conditions is roughly three orders of magnitude greater than that of the corresponding liquid. As a result the quantity $\Delta s/\Delta v$ is always smaller for the liquid-to-vapor than the crystal-to-liquid transtion.

There are different kinds of phase diagrams. As a useful example, we provide the pressure-temperature diagram, but with axes flipped so that the pressure is now the horizontal axis, and, alongside, the corresponding diagram where the horizontal axis is the concentration. The latter one is quite a bit more informative as it gives a better sense of phase coexistence:



The so called triple point is the point on the phase diagram where the three phase boundaries—liquid-vapor, liquid-Xtal, and vapor-Xtal, respectively—cross. A single-component substance can have at most one triple point (Gibbs phase rule). The \tilde{G} function has three minima at the triple point. In general, already a pure substance can a very substantial number of phases. Phase diagrams of mixtures can become mind-bogglingly complex. In addition, there is still a possibility that there is phase that is not stable under any conditions but can be kinetically accessible. These rich phenomena are subject of Materials Science.

Finally, we can use Eq. 8 and the relation between the Gibbs and Helmholtz free energy, $G = A + pV$, to relate the Helmholtz free energy change during the transition to the corresponding volume change:

$$(23) \quad \Delta G = \Delta(A + pV) = 0 \Rightarrow \Delta A = -p\Delta V$$

We observe that the Helmholtz free energy always decreases for a transition incurring a volume increase. Moreover, the magnitude of this decrease is exactly equal to the work needed to expand the system to the new

value of the volume. This is consistent with our earlier conclusion that the amount of mechanical work one can extract at constant temperature should match the decrease of the Helmholtz free energy.

The above equation should have been obvious already from Figure 6, where, we see, $p_0 = -\frac{A_2 - A_1}{V_2 - V_1} = -\frac{\Delta A}{\Delta V}$. There is a useful consequence of this fact. Indeed, we just established that

$$(24) \quad A_2 - A_1 = -p_0(V_2 - V_1)$$

On the other hand, since $p = -(\partial A / \partial V)$ for the non-equilibrium isotherm,

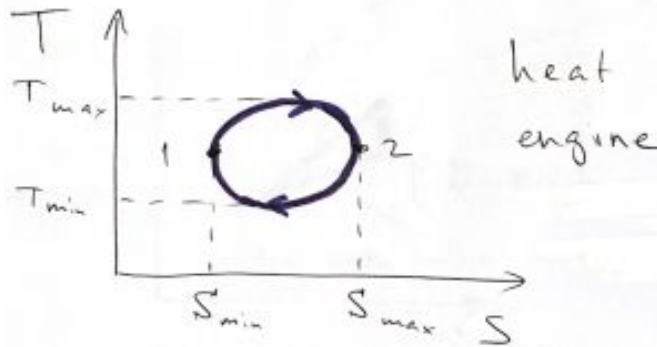
$$(25) \quad A_2 - A_1 = - \int_{V_1}^{V_2} p \, dV$$

Thus the areas under the equilibrium and non-equilibrium isotherms, in the $[V_1, V_2]$ interval, are exactly equal to each other. This implies that the two shaded regions in Fig. 7 must have the same area, too. This, then, allows one to determine the equilibrium pressure of the transition if a non-equilibrium isotherm is known, without having to explicitly compute the Helmholtz free energy as a function of volume and determining the common tangent. This recipe is known as “the Maxwell construction.”

9.

Heat Engines. Refrigeration.

An important application of Thermodynamics and, arguably, the one that had motivated its systematic development in the first place, is Heat Engines. By construction, a heat engine consists of a working body, such as a gas or a mixture of vapor and liquid, that undergoes a cyclic process. During each cycle, heat that had been produced by some means is imparted to the working body. (The heat can be produced by burning a fuel, or a nuclear reaction, or by absorbing sunlight, etc.) Some of this heat is converted into useful work and some heat goes back in the environment. The temperature and entropy both vary during the cycle. We can graphically depict this state of affairs using the following graph:



We have chosen the direction in the above process quite deliberately: The high-temperature, $1 \rightarrow 2$ leg of the process corresponds to inputting heat, while during the low temperature, $2 \rightarrow 1$ leg, heat is extracted from the system. Under these circumstances, the net heat put into the system is positive:

$$(1) \quad \oint \delta Q > 0$$

Indeed, the cyclic integral above can be presented as the sum of the integral along the $1 \rightarrow 2$ leg and the $2 \rightarrow 1$ leg:

$$(2) \quad \oint \delta Q = \int_1^2 \delta Q + \int_2^1 \delta Q = \int_1^2 T dS + \int_2^1 T dS$$

where we note that in the 1st integral in the r.h.s., $dS > 0$, and in the 2nd integral, $dS < 0$, because in the latter integral the argument decreases when going from the initial point of integration to the final point of integration. We next re-write the integrals so that the integration boundaries correspond with the numerical values of the argument at the left and right edge of the integration range, while being careful to specify the temperature along each leg:

$$(3) \quad \int_1^2 T dS = \int_{S_{\min}}^{S_{\max}} T_{1 \rightarrow 2} dS$$

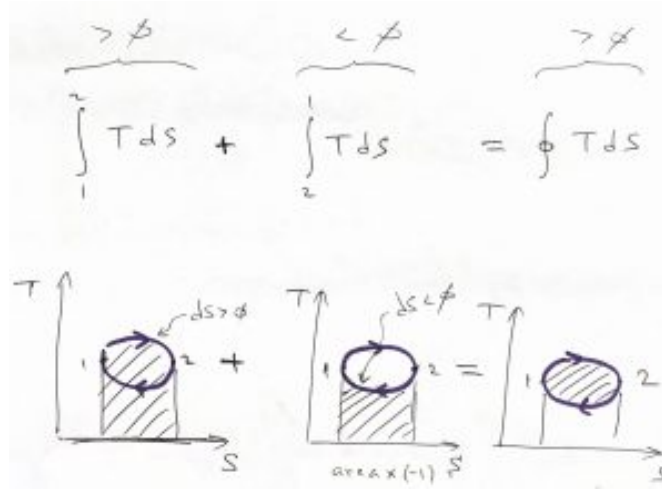
By construction, $S_{\min} < S_{\max}$. Likewise,

$$(4) \quad \int_2^1 T dS = \int_{S_{\max}}^{S_{\min}} T_{2 \rightarrow 1} dS = - \int_{S_{\min}}^{S_{\max}} T_{2 \rightarrow 1} dS$$

Adding Eqs. 3 and 4

$$(5) \quad \oint \delta Q = \int_1^2 \delta Q + \int_2^1 \delta Q = \int_1^2 T dS + \int_2^1 T dS = \int_{S_{\min}}^{S_{\max}} (T_{1 \rightarrow 2} - T_{2 \rightarrow 1}) dS > 0$$

since for each value of entropy, $T_{1 \rightarrow 2} > T_{2 \rightarrow 1}$, by construction, and $dS > 0$ in the above integral. This notion can be illustrated graphically since the integral from left to right of a positive function is simply the area under the curve, while the integral of a positive function from right to left is equal to the area under the respective curve times the minus sign:



The fact of the total heat input being positive is key. To see this, integrate the differential form of energy conservation

$$(6) \quad dE = \delta Q - \delta W$$

along the cycle:

$$(7) \quad \oint dE = \oint \delta Q - \oint \delta W$$

and note that the cyclic integral of the energy is equal to zero because, on the one hand, the integral of dE yields ΔE for the process and, on the other hand, the energy is a state function. The value of a state function is fully determined by the values of the control variables irrespective of the preparation protocol of the system. Since the initial and final states for cyclic processes are identical, $\Delta E = 0$. Hence,

$$(8) \quad \oint dE = 0$$

and so we obtain that the work done by system is exactly equal to the total amount of heat absorbed by the working body:

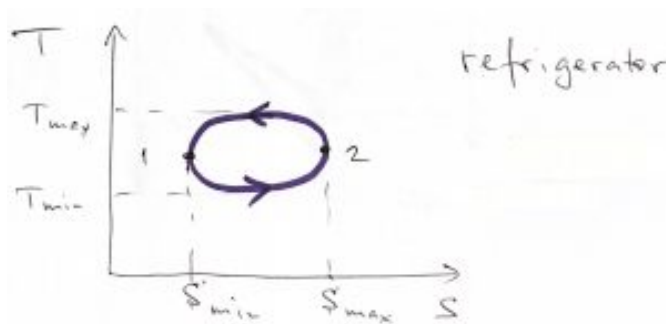
$$(9) \quad \oint \delta W = \oint \delta Q$$

This equation can be regarded as a form of energy conservation law and implies that one cannot extract useful work out of nothing. Hypothetical engines that could do the latter, are called engines of the 1st kind. Clearly, such engines are physically impossible. Whenever there is an impression that work is created out of nothing, there a source of energy unaccounted for.

This simple and important result in 9 also presents an opportunity to explain why we have used the symbol

δ to denote small amounts of heat and work exchange, not the symbol “d”. This is to emphasize that heat and work are not state functions and how much heat or work has been exchanged with the systems actually depends on the specifics of the process, not just the initial and final states of the process. Here, specifically, we observe that neither δQ nor δW individually corresponds to an increment of a function, but their difference, $\delta Q - \delta W = dE$, does in fact correspond to an increment of a state function. One may also say that while one can ask how much energy a system has, one cannot ask how much heat (or work) the system has, only how much heat or work has been exchanged with the system during a specific process.

Eq. 9 is valid whether we go around the cycle clockwise or counterclockwise. In the former case, both integrals are positive, while in the latter, both integrals are negative. What type of machine does the *counterclockwise* process correspond to?



The negative work by the system means somebody *else* performs positive work on the system. At the same time, the negative $\oint \delta Q$ implies that the heat is imparted to the working body on the low temperature leg of the process and is extracted from the working body on the high temperature leg of the process. This state of affairs corresponds to *refrigeration*.

Thus the very same machine can be used both as an engine or a refrigerator depending on the directionality of the process. In practice, the engines work on much faster times scales than refrigerators and so one ordinarily employs distinct physical processes for the respective machines. Heat engines usually operate using hot gases. Although not particularly caloric in nature, expansion and compression of a gas can be done on rapid time scales thus allowing one to produce large amounts of power. For refrigerators, the power by itself is not of great priority. Instead, here one usually employs mechanical agitation or expansion to evaporate a liquid, which is in contact with the object or place that needs to be cooled. Evaporation extracts heat from that place. The vapor is then transported to elsewhere, where it condenses and gives off some of that heat. The liquid is then mechanically brought back in contact with the refrigerated object and so on. The power required to induce the evaporation is not particularly large, but the amount of heat involved in evaporation/condensation is substantial enough so that relatively small heat exchange units suffice to cool your home during hot Summer days.

Now, the efficiency of the heat engine is judged by which fraction of the heat imparted to the engine converted to useful work. Indeed, as far as the engine is concerned, the heat given off by the working body is not used to perform work by the engine itself. (This heat can be, in principle, collected and utilized.) Thus we define efficiency as

$$(10) \quad \eta \equiv \frac{\oint \delta W}{\int_1^2 \delta Q}$$

which, by virtue of Eq. 9, becomes

$$(11) \quad \eta \equiv \frac{\oint \delta Q}{\int_1^2 \delta Q}$$

This can be expressed more vividly as the ratio of the following two areas:

$$\eta \equiv \frac{\oint \delta w}{\oint \delta q} = \frac{\oint \delta q}{\oint \delta q} = \frac{T}{s} < 1$$

Because $\oint \delta Q = \int_1^2 \delta Q + \int_2^1 \delta Q < \int_1^2 \delta Q$, the efficiency is generally less than one but can be improved by lowering the temperature of the heat sink, i.e., the temperature at which the working body gives off heat, so as to make the quantity $\int_2^1 \delta Q = \int_2^1 T dS$ smaller in magnitude. It turns out that there is an intrinsic upper bound on the efficiency of a heat engine, as elucidated by the French engineer Sadi Carnot some 200 years ago. To establish this bound, we first state an upper bound on the heat that can be passed on to the system at temperature T during an elemental process, known as the **Clausius inequality**:

$$(12) \quad \delta Q \leq T dS_{\text{eq}}$$

where dS_{eq} is the eventual, equilibrium entropy change resulting from the process. The equality refers to the case when the system was, in fact, in equilibrium with the environment throughout the process, while the inequality covers situations where the process is faster than the relaxation time of the system.

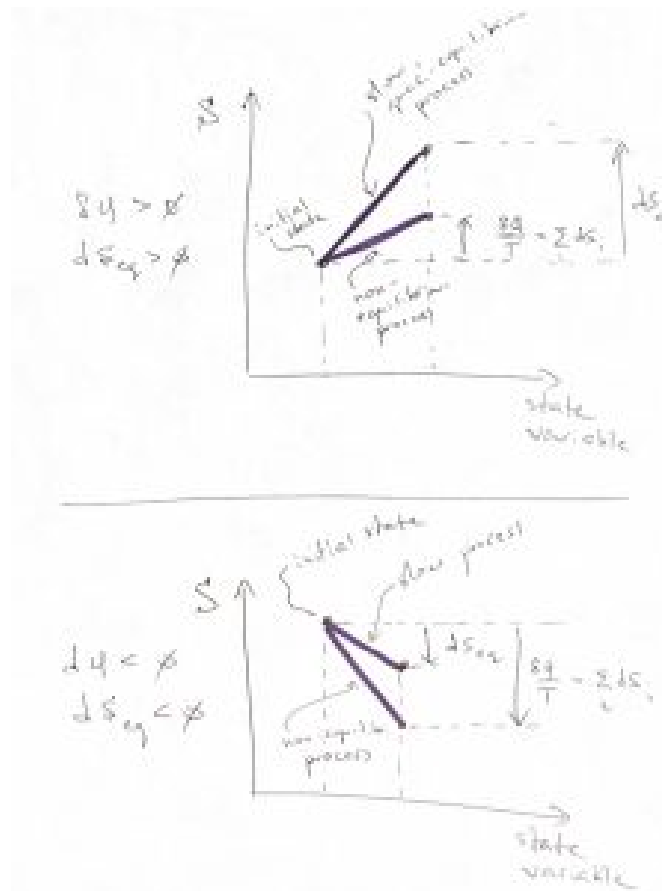
The Clausius inequality comes about in the following way: Imagine the body has just received some heat in a process that is not necessarily quasi-static, in which case the body is not fully equilibrated. We can mentally subdivide the body into smaller parts, each of which still contains many molecules, but are small enough that it can be regarded as equilibrated. Thus the total amount of heat passed on to the system can be broken up into components δQ_i , for each of which we can use the equilibrium expression $\delta Q_i = T dS_i$, and so:

$$(13) \quad \delta Q = \sum_i T dS_i = T \sum_i dS_i$$

Suppose $\delta Q > 0$ and, thus, so are dS_i . In this case, the sum of the increments is maximized when the final value of $\sum_i S_i$ is maximized. But $\sum_i S_i$ is the total entropy the body, which achieves its maximum value in equilibrium:

$$(14) \quad \delta Q = T \sum_i dS_i \leq T dS$$

The $\delta Q < 0$ case can be treated similarly and gives the same result, as we graphically illustrate below:



Upon dividing [12](#) by T and integrating along a cyclic process, one obtains the integral form of the Clausius inequality:

$$(15) \quad \oint \frac{\delta Q}{T} \leq 0$$

because the equilibrium value of entropy is a state function and so $\oint dS_{eq} = 0$.

We can use Eq. [15](#) to place certain bounds on the heat exchange with the system along the high temperature and low temperature legs of the cyclic process:

$$(16) \quad \int_1^2 \frac{\delta Q}{T} \geq \int_1^2 \frac{\delta Q}{T_{max}} = \frac{1}{T_{max}} \int_1^2 \delta Q = \frac{Q_{1 \rightarrow 2}}{T_{max}}$$

since $T < T_{max}$. Likewise,

$$(17) \quad \int_2^1 \frac{\delta Q}{T} \geq \int_2^1 \frac{\delta Q}{T_{min}} = \frac{1}{T_{min}} \int_2^1 \delta Q = \frac{Q_{2 \rightarrow 1}}{T_{min}}$$

since δQ is negative on this leg of the process and $T > T_{min}$. Adding these two inequalities yields:

$$(18) \quad \frac{Q_{1 \rightarrow 2}}{T_{max}} + \frac{Q_{2 \rightarrow 1}}{T_{min}} \leq \int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q}{T} \equiv \oint \frac{\delta Q}{T} \leq 0$$

Where we used the Clausius inequality in the last step. In turn, this implies

$$(19) \quad \frac{Q_{2 \rightarrow 1}}{Q_{1 \rightarrow 2}} \leq -\frac{T_{min}}{T_{max}}$$

and, finally,

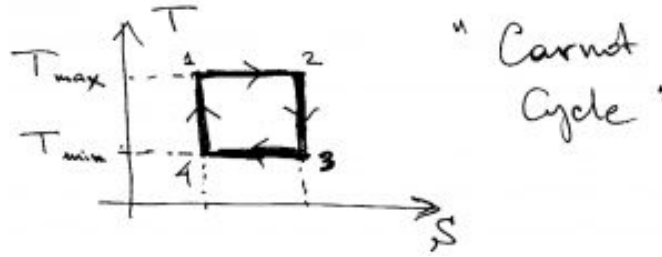
$$(20) \quad \eta \equiv \frac{\oint \delta Q}{\int_1^2 \delta Q} = \frac{Q_{1 \rightarrow 2} + Q_{2 \rightarrow 1}}{Q_{1 \rightarrow 2}} = 1 + \frac{Q_{2 \rightarrow 1}}{Q_{1 \rightarrow 2}} \leq 1 - \frac{T_{\min}}{T_{\max}}$$

or,

$$(21) \quad \eta \leq \frac{T_{\max} - T_{\min}}{T_{\max}}$$

To summarize, the quantity on the r.h.s. represents a fundamental upper bound on the efficiency of a (one-stage) heat engine. Note *other* sources of loss are present, such as friction between moving parts or incomplete burning of the fuel. This fundamental upper bound is intrinsically less than one, since the absolute zero of temperature, $T_{\min} = 0$, is not achievable. A hypothetical engine that would convert all of the heat into useful work is called the heat engine of the 2nd kind. Carnot's result, then, demonstrates that the engine (or "perpetual motion") of the 2nd kind is impossible. This notion is yet another equivalent formulation of the 2nd Law of Thermodynamics.

The natural question is, then: Aside from those additional losses, is there a process where the maximum possible value of η , i.e. $\frac{T_{\max} - T_{\min}}{T_{\max}}$, is in fact achieved? Upon inspection of Eqs. 16 and 17 we readily conclude that the equality in those two equations are achieved when $T = T_{\max}$ throughout the high temperature leg, and $T = T_{\min}$ throughout the low temperature leg. This is achieved only in the following cycle, which is called the "Carnot cycle":

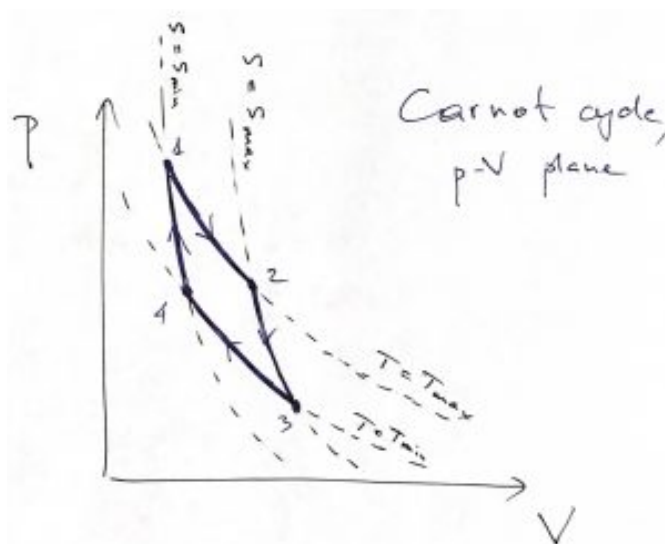


That is, the temperature should actually stay constant during heating exchange. It is instructive to re-plot this cycle in the pressure-volume plane, to see where the working body expands and where it contracts. In the (p, V) plane, the cycle looks more complicated because the straight lines connecting the corners of the rectangle in the (T, S) plane become curved lines in the (p, V) plane. Indeed, the isotherm $T = T_{\min}$ becomes $p = Nk_B T_{\min}/V$, the isotherm $T = T_{\max}$ becomes $p = Nk_B T_{\max}/V$. The isentropes $S = S_{\min}$ and $S = S_{\max}$ become curves along each of which the quantity $pV^{\frac{c_V+1}{c_V}}$ remains constant. This is made apparent by setting $S = \text{const}$ in the expression for the entropy we had obtained earlier:

$$(22) \quad S(T, V) - S(T^\ominus, V^\ominus) = C_V \ln \left(\frac{T}{T^\ominus} \right) + Nk_B \ln \left(\frac{V}{V^\ominus} \right)$$

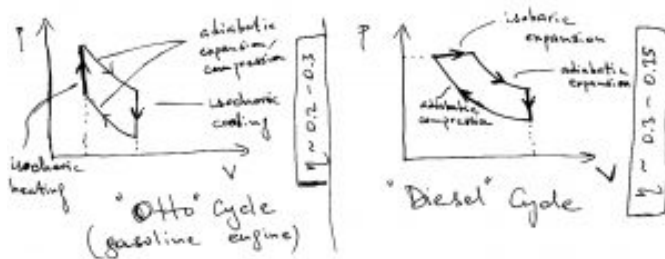
and using the ideal gas law $pV = Nk_B T$.

One can convince oneself that if an isentrope and isotherm intersect at some point (V_0, p_0) , the isentrope always have a steeper slope than the isotherm, because $\frac{c_V+1}{c_V} > 1$. Thus we arrive at the following picture for the Carnot cycle in the (p, V) plane:



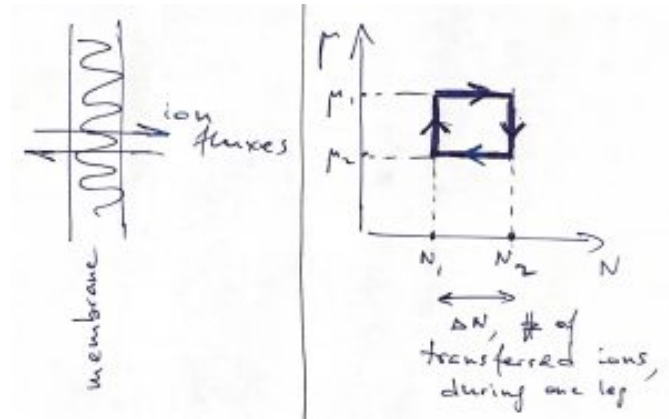
Thus we directly see that the system does useful work on the $1 \rightarrow 2$ leg, where it expands isothermally and absorbs heat, and on the $2 \rightarrow 3$ leg, where it expands isentropically, i.e., without heat exchange with the environment, and, thus, cools. On the $3 \rightarrow 4$ leg, the system contracts and gives off heat while staying at the temperature of the heat sink, while in the final, $4 \rightarrow 1$ leg, the system keeps contracting without heat exchange and, thus, warms back up to the temperature of the heat source.

Actual engines do not operate via the Carnot cycle for practical reasons, for which reason they are less efficient than what is prescribed by Carnot's upper bound. (This is in addition to a variety of aforementioned mechanical and chemical losses.) Examples of those other types of engines are given below for your reference:



We note that since the electronic energies, which are of order eV, are much higher than the thermal energy scale, electrical engines operate much more efficiently than heat engines. Thus, in principle, if one can convert sunlight into electricity with relatively little heat dissipation, we can make convert energy into work in a drastically more efficient way. We know that absorption of light by molecules is accompanied by some vibrational relaxation, which leads to dissipation of energy. In any event, the best man-made photovoltaic devices can operate at 40% efficiency. Perhaps, plants can do it better.

Finally, we mention that these ideas can be applied to types of work other than mechanical work. Imagine, for instance, recurrent shuttling of ions across the membrane of a living cell or a mitochondrion:



Here, one may consider a cyclic process where the temperature is kept constant, and so the appropriate thermodynamic potential is the Helmholtz free energy: $dA = -p dV + \mu dN$, ($dT = 0$). Hereby one can extract mechanical work $\oint \delta W = \oint p dV = \oint \mu dN$, if the ions diffuse back and forth in a cyclic fashion while the two sides of the membrane are maintained at different values of the chemical potential. Conversely, one may induce ion transfer by mechanically moving the interface.

10.

Thermochemistry. Detailed balance.

Of great direct importance to chemists and biologists is the branch of Thermodynamic that deals with chemical equilibrium. This will be the first time we face a situation where a particle can split into two or more particles which, automatically, have difference properties. Likewise, two or more particles, be they distinct or not, can transiently bind to form something a new species. Both of these processes are generally present and cannot be stopped, in fact. The question is, then, whether the composition will ever become steady-state. If yes, what controls the steady-state composition? Will the chemical process proceed in the direction we expect it to, say, formation of another molecule of practical significance, or will the reaction not occur?

First off, we need to generalize the definition of the free energy to include the possibility that there are more than one kind of particles, i.e., chemical species, in the system. In most cases, we are interested in chemical reactions at constant pressure and temperature, and so the appropriate free energy is that due to Gibbs:

$$(1) \quad dG = -SdT + Vdp + \sum_i \mu_i dN_i$$

where, by construction, the chemical potential of species i is the free energy cost of adding one particle of species i , while keeping pressure, temperature, and the amount of the other species constant:

$$(2) \quad \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{p, T, N_{j \neq i}}$$

While we'll concentrate on $p, T = \text{const}$ conditions, other types of conditions can be described analogously using appropriate thermodynamic potentials. To give a few examples:

$$(3) \quad \mu_i = \left(\frac{\partial E}{\partial N_i} \right)_{S, V, N_{j \neq i}} = \left(\frac{\partial A}{\partial N_i} \right)_{V, T, N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i} \right)_{S, p, N_{j \neq i}}$$

The Gibbs free energy of a mixture has an important property of being a sum of the chemical potentials of the constituents, each multiplied by the corresponding particle number:

$$(4) \quad G = \sum_i^M \mu_i N_i$$

where the summation is over the distinct species, of which there are M . To see this, we first note that

$$(5) \quad G(p, T, N_1, N_2, \dots, N_M) = N g(p, T, x_1, x_2, \dots, x_M)$$

where $N = \sum_i N_i$ is the total particle number and $x_i \equiv N_i/N$ is the mole fraction of species i . Thus,

$$(6) \quad \left(\frac{\partial G}{\partial N} \right)_{p, T, x_i} = g(p, T, x_1, x_2, \dots, x_M) = \frac{G}{N}$$

On the other hand, the Gibbs energy depends on N exclusively through the partial quantities N_i , and so we obtain, using the chain rule of differentiation while setting $p, T = \text{const}$:

$$(7) \quad \left(\frac{\partial G}{\partial N} \right)_{p,T,x_i} = \sum_i \left(\frac{\partial G}{\partial N_i} \right)_{p,T,x_{j \neq i}} \left(\frac{dN_i}{dN} \right)_{x_i} = \sum_i \mu_i \frac{N_i}{N}$$

where we used $(\partial G / \partial N_i)_{p,T,N_{j \neq i}} \equiv \mu_i$ and $(dN_i / dN)_{x_i} = [d(x_i N) / dN]_{x_i} = x_i = N_i / N$. Note that although the chemical potentials do not contain any information as to the total size of the system or the total quantity of the components, they do generally depend on the *partial* quantities x_i of the components. We will see concrete examples of this shortly.

It will be convenient in this Chapter to work with moles, not particle numbers. To make the switch we first note that

$$(8) \quad \mu_i N_i = \mu_i N_A \frac{N_i}{N_A} \equiv \mu_i N_A n_i$$

where $n_i \equiv N_i / N_A$ is thus the number of moles of species i . For this Chapter, we re-define the chemical potential to be per mole:

$$(9) \quad \mu_i N_A \rightarrow \mu_i$$

so that the units are now J/mol. Because the letter n is now used to denote the number of moles, we will be using not the letter n for the concentration but, instead, for the species name enclosed in square brackets, as it is often done in Chemistry textbooks.

With the above definitions, we obtain:

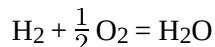
$$(10) \quad dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

and

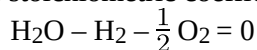
$$(11) \quad G = \sum_i^M \mu_i n_i$$

This equation—like the Eq. 4—is an example of Hess's Law, by which the total thermodynamic potential or entropy of a mixture is equal to the sum of the partial contributions of the individual species weighted by the respective amounts. Again, it is important to realize that those individual contributions are affected by the presence of the other species, if any, and are not generally equal to their values for the respective pure substances.

A conventional way to write down a chemical reaction is to place the reactants on one side of the equation and the products on the other side. For instance, the process where molecular hydrogen and oxygen combine to form water and the reverse process where water dissociates to form molecular hydrogen and oxygen can be written like this:



To avoid ambiguity as to what we consider products and what reactants, we will group all the component names on one side of the equation (and leaving zero on the other side), where the stoichiometric coefficient for the products are, by construction, positive, and the stoichiometric coefficient for the reactants are negative:



We shall use the Greek letter ν_i to denote the stoichiometric coefficient for species i . Thus for the reaction above:

$$\begin{aligned} \nu_{\text{H}_2\text{O}} &= +1 \\ \nu_{\text{H}_2} &= -1 \\ \nu_{\text{O}_2} &= -1/2 \end{aligned}$$

With this convention, it is straightforward to quantify the progress of the reaction with just one variable called the *progress coordinate* or *progress variable*, because the consumption of reactants and the production of products are strictly related. For instance, in the above reaction, for each mole of H_2 and half-mole of O_2 consumed, one

mole of H_2O is produced. We shall use the Greek letter ξ for the progress variable and have it that $\xi = 0$ if no reaction has proceeded, i.e., no reactants have been used up:

$$(12) \quad n_i = n_{i,0} + \nu_i \xi$$

where $n_{i,0}$ is the number of moles of species i in the beginning of the process or in some standard state. By construction, then, ξ attains its largest possible value once the reaction has fully completed.

Our next task is to determine the equilibrium value of ξ , i.e., the extent to which the reaction will proceed, if at all. To do so, we recall that the Gibbs free energy must reach its lowest possible value in equilibrium. Inserting Eq. 12 in the expression 10 for the Gibbs free energy, we thus obtain the increment of the familiar thermodynamic potential \tilde{G} , which is now an explicit function of the progress coordinate ξ :

$$(13) \quad d\tilde{G} = -SdT + Vdp + \left(\sum_{i=1}^M \nu_i \mu_i \right) d\xi$$

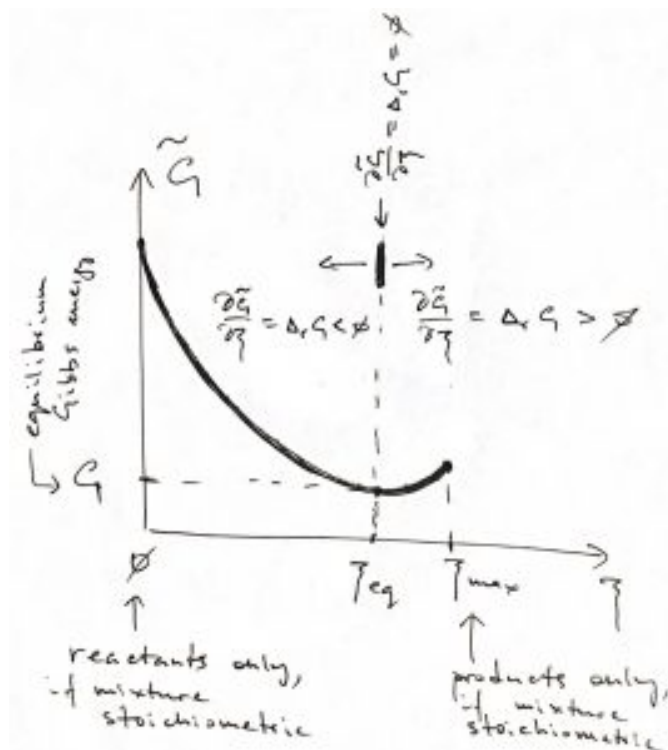
and the quantity in the brackets is called the Gibbs energy of the reaction, not to be confused with the Gibbs energy of the system:

$$(14) \quad \Delta_r G \equiv \sum_{i=1}^M \nu_i \mu_i$$

By Eq. 13, the Gibbs energy of the reaction is the derivative of the (non-equilibrium) Gibbs free energy \tilde{G} with respect to the progress coordinate

$$(15) \quad \left(\frac{\partial \tilde{G}}{\partial \xi} \right)_{T,p} = \Delta_r G$$

Since the equilibrium value of the Gibbs energy corresponds to the minimum of \tilde{G} ,



the equilibrium value of ξ corresponds with $\Delta_r G = 0$. Furthermore, if the reactive mixture happens to have been prepared away from the equilibrium composition, the direction of the process will be determined by the sign

of $\Delta_r G$, since for $\xi < \xi_{\text{eq}}$, $\Delta_r G < 0$, and so ξ will be increasing until it reaches its equilibrium value and vice versa for $\xi > \xi_{\text{eq}}$. We summarize these notions in the Table below:

$\Delta_r G < 0$	$d\xi > 0$	reaction will proceed as written
$\Delta_r G > 0$	$d\xi < 0$	reaction will proceed in the opposite direction
$\Delta_r G = 0$	$d\xi = 0$	the reactive mixture is already at equilibrium

It is straightforward to obtain explicit expression for the Gibbs free energy of a gas reaction in the approximation of the gases being nearly ideal. We will use the expression for the chemical potential we had obtained in Chapter 7, which we re-write here per mole:

$$(16) \quad \mu = -RT \ln \left[\left(\frac{T}{eT^\ominus} \right)^{c_V/k_B} \left(\frac{V}{V^\ominus} \right) \right]$$

To make it a function exclusively of temperature and pressure, we will use the ideal gas law $pV = Nk_B T$ and standard formulas $x \ln y = \ln y^x$ and $\ln x + \ln y = \ln(xy)$ to obtain $\mu = RT \ln(p T^{-c_V/k_B-1} \times \text{const})$, where the constant depends on the standard pressure and temperature and, also, contains numerical factors. In much of the following, we will set the temperature to its standard value, which, then, yields a greatly simplified expression for the chemical potential:

$$(17) \quad \mu = \mu^\ominus + RT \ln(p/p^\ominus)$$

Note that this expression can be used to evaluate the chemical potential of the gas when the gas is part of a gas mixture but p now stands for the *partial* pressure of the gas in the mixture. Indeed, Eq. 16 contains the full volume of the system, and so the equation of state $p_i = N_i k_B T / V$, where N_i is the particle number for component i , gives the pressure due to the component i exclusively, irrespective of whether other components are present or not.

Now consider, for the sake of argument, the very simplest reaction



and assign species B to be the product and species A the reactant:



Thus

$$\nu_A = 1 - \xi$$

and

$$\nu_B = \xi$$

Assume further that this is a gas reaction and that the gases are nearly ideal. If the total pressure is p , the partial pressures of the species A and B, respectively, are given by:

$$(18) \quad p_A = \frac{\nu_A}{\nu_A + \nu_B} p = (1 - \xi) p$$

and

$$(19) \quad p_B = \frac{\nu_B}{\nu_A + \nu_B} p = \xi p$$

because $p_A = N_A k_B T / V$ and $p_B = N_B k_B T / V$, while $p = (N_A + N_B) k_B T / V$. Note that the chemical potentials of both species A and B depend on the mole fractions of the components, as was alluded to earlier.

Substituting the partial pressures in the respective expressions for the chemical potentials in Eq. 10, one obtains the following expression for the overall (non-equilibrium) Gibbs energy:

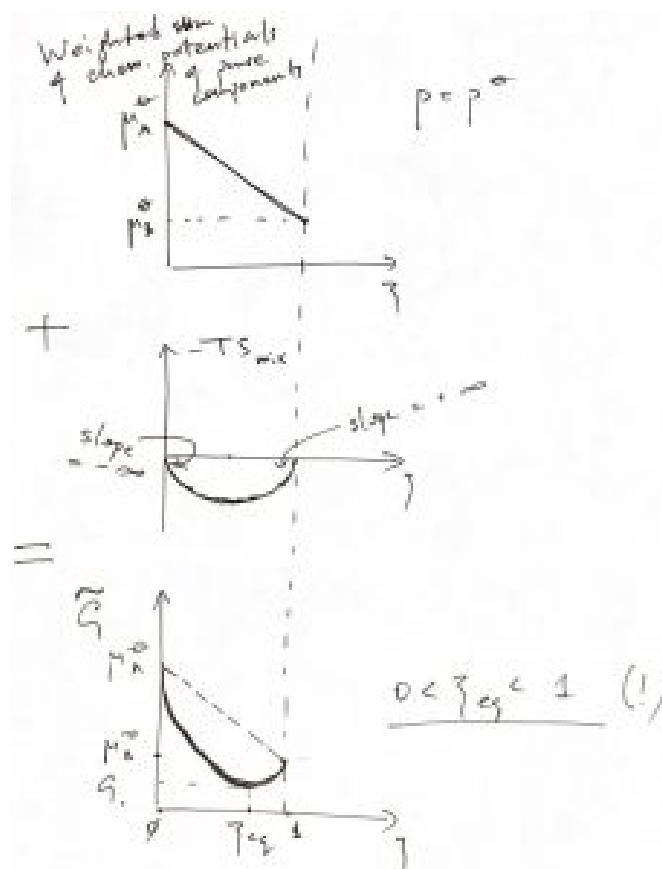
$$\begin{aligned}
 \tilde{G} &= n_A \mu_A + n_B \mu_B \\
 (20) \quad &= (1 - \xi)[\mu_A^\ominus + RT \ln(p_A/p^\ominus)] + \xi[\mu_B^\ominus + RT \ln(p_B/p^\ominus)]
 \end{aligned}$$

thus leading to

$$(21) \quad \tilde{G} = \mu_A^\ominus + \xi(\mu_B^\ominus - \mu_A^\ominus) + RT \ln(p/p^\ominus) + RT[\xi \ln \xi + (1 - \xi) \ln(1 - \xi)]$$

In this expression, we recognize the last term as that arising from the entropy of mixing: $-TS_{\text{mix}}$. One can easily check that the remaining terms are a weighted sum of the chemical potentials of *pure* species A and B, respectively, the weights determined the corresponding mole fractions.

The mixing contribution has an important mathematical property that its derivatives are infinite at the l.h.s. and r.h.s. edges of interval of allowed values of ξ . At the same time, the slope of the remaining ξ dependence is finite throughout. This implies that the minimum of the non-equilibrium Gibbs energy is necessarily contained *within* the interval.



This means that the reaction always proceeds at least to some extent but, at the same time, never proceeds to full completion! This interesting entropic effect comes about, physically, because no matter how unfavorable the reactants or products might be, once formed they will have the whole volume of the system at their disposal. For this very reason, it is very hard to purify a substance or, for instance, fully eliminate crime in a large city. On the good side, it also means that a large city is essentially guaranteed to have exceptionally good people, too!

By analogy with the expression for the chemical potential of an ideal gas of species i

$$(22) \quad \mu_i = \mu_i^\ominus + RT \ln(p_i/p^\ominus)$$

be the species in pure form or a part of a gaseous mixture, we use the following formal expression for the chemical potential of species i in *any* physical form:

$$(23) \quad \mu = \mu_i^\ominus + RT \ln a_i$$

where the quantity a_i is called the *activity*. To reiterate,

$$(24) \quad a_i = p_i/p^\ominus \text{ for ideal gases}$$

For non-ideal gases, on the other hand, $a_i = \gamma_i p/p^\ominus$, where γ is called the fugacity coefficient (the combination γp is called the fugacity) and p is the total pressure. Note that for non-ideal gases, one can no longer define partial pressures since distinct components now interact. For liquid mixtures, we take the respective pure substances as the standard states, and so, by definition, $a_i = 1$ in the standard state. The rationale behind the convention 23 is not solely formal: In the limit of low mole fraction of the species i one can think of it as a dilute “gas” of molecules of this species while the rest of the liquid mixture can be thought of as an effective vacuum that can be described effectively as a vacuum but with somewhat distinct properties from the actual vacuum. Since the molecules of this effective “gas” do not interact with each other, we expect the activity to scale linearly with its concentration

$$(25) \quad a_i \propto [i], \text{ at low values of concentration } [i]$$

as if the species were a nearly ideal gas.

It is instructive to express the reaction’s Gibbs energy through the activities:

$$\begin{aligned}
 \Delta_r G &\equiv \sum_{i=1}^M \nu_i \mu_i \\
 &\equiv \sum_{i=1}^M \nu_i (\mu_i^\ominus + RT \ln a_i) \\
 &= \sum_{i=1}^M \nu_i \mu_i^\ominus + RT \sum_{i=1}^M \nu_i \ln a_i \\
 &= \Delta_r G^\ominus + RT \ln \prod_{i=1}^M a_i^{\nu_i} \\
 (26) \quad &= \Delta_r G^\ominus + RT \ln Q
 \end{aligned}$$

where we have defined the standard Gibbs energy of the reaction

$$(27) \quad \Delta_r G^\ominus \equiv \sum_{i=1}^M \nu_i \mu_i^\ominus$$

and the so called **reaction quotient**

$$(28) \quad Q \equiv \prod_{i=1}^M a_i^{\nu_i}$$

The reaction quotient looks like a rather formal object yet it is the only systematic way to quantify the balance between the reactants and products. For instance, consider the dilute limit of the gas reaction $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$. Hereby, the activity of each component is proportional to its concentration, and so $Q \propto \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$, which makes perfect sense: The chances of the reaction proceeding in the direction as written is determined by the

probability of bringing together two hydrogen molecules and one oxygen molecule, which is proportional to the product $[H_2][H_2][O_2] = [H_2]^2[O_2]$. (Recall that the probabilities of independent events multiply and that the concentration of the molecule is proportional to the probability to find that molecule.) On the other hand, since the reaction produces two water molecules, the probability of the reverse process is determined by the chances of bringing together two water molecules. Thus the proper measure of the probability to be in the “product state” of the system relative to the “reactant state of the system” is given by the reaction quotient.

What is the equilibrium value of the reaction quotient? According to the Table above, the reactive mixture is in equilibrium, if $\Delta_r G_r = 0$. Thus, by Eq. 26, we have at equilibrium

$$(29) \quad \Delta_r G^\ominus + RT \ln Q_{eq} = 0$$

The equilibrium value of the reaction constant is rather special and has its own name: **the equilibrium constant**:

$$(30) \quad K \equiv Q_{eq}$$

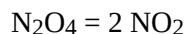
Thus we obtain that the equilibrium constant, i.e., the equilibrium value of the reaction quotient has the following relation with the standard Gibbs free energy:

$$(31) \quad K = e^{-\Delta_r G^\ominus / RT}$$

Not surprisingly, we obtain that the probability of being in the product relative to reactant state is given by the relative Boltzmann weight of the two states, in complete consonance with our developments so far.

Note that to each value of temperature there corresponds a unique value of the equilibrium constant. Moreover, the equilibrium constant is exclusively a function of temperature, but not pressure since the standard pressure is fixed, by convention.

The above notions can be used to analyze the pressure dependence of the chemical equilibrium. As an example, consider the following simple gas reaction, where a weak complex N_2O_4 (reversibly) falls apart into two identical molecules NO_2 :



According to Eq. 12, $n_{NO_2} = 2\xi$, and $n_{N_2O_4} = 1 - \xi$ while the total amount is $2\xi + (1 - \xi) = 1 + \xi$. Thus:

	N_2O_4	NO_2
initial amount	1	0
equilibrium amount	$1 - \xi_{eq}$	$2 \xi_{eq}$
equilibrium mole fraction	$\frac{1 - \xi_{eq}}{1 + \xi_{eq}}$	$\frac{2 \xi_{eq}}{1 + \xi_{eq}}$
partial pressure in equilibrium	$p_{NO_2} = \frac{1 - \xi_{eq}}{1 + \xi_{eq}} p$	$p_{N_2O_4} = \frac{2 \xi_{eq}}{1 + \xi_{eq}} p$

where p is the total pressure: $p = p_{NO_2} + p_{N_2O_4}$. This yields for the equilibrium constant, after simple algebra:

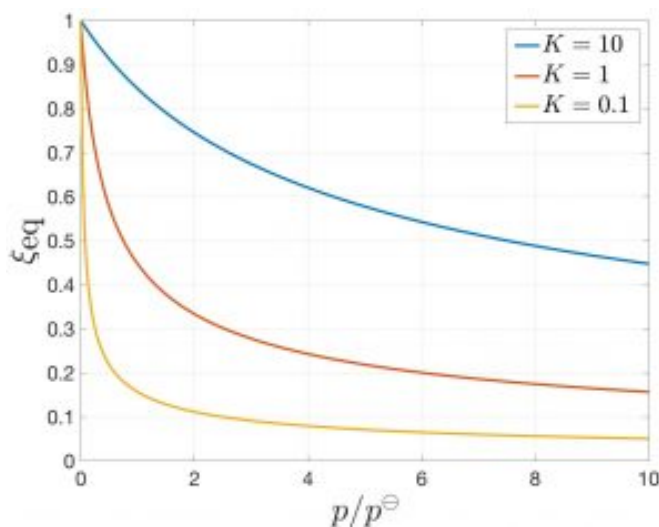
$$\begin{aligned}
 K &= \frac{(p_{NO_2}/p^\ominus)^2}{p_{N_2O_4}/p^\ominus} \\
 &= \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} \frac{p}{p^\ominus}
 \end{aligned}
 \quad (32)$$

The relation between the equilibrium constant and the equilibrium value of the reaction coordinate we just

obtained happens to be simple enough that we can solve it for ξ_{eq} in terms of pressure and the equilibrium constant:

$$(33) \quad \xi_{\text{eq}} = \frac{1}{[1 + \frac{4}{K} \frac{p}{p^\ominus}]^{1/2}}$$

We plot it here as a function of pressure for three select values of K :



Clearly, the amount of products decreases with pressure. This is expected since the volume of the product is greater than the volume of the reactants, per mass. Thus one can shift the equilibrium toward reactants by increasing the pressure and toward products by reducing the pressure. This is an example of the Le Chatelier principle, whereby the system responds so as to compensate the external influence. Indeed, by reducing the volume of the mixture, the system “mitigates” our attempt to increase its pressure. We also see the amount of products increases with the equilibrium constant, as expected.

In addition to the direction of a chemical process, of interest is also the heat, or, *enthalpy* of the reaction since it determines how much heat will be produced or consumed during the reaction. In the former case, one must be able to sequester the heat to avoid explosion while in the latter case, one must supply heat in order for the reaction to take place. Note that in either case, the kinetics are important because what matters is how much heat is produced/consumed in unit time. Here we are mostly concerned with the thermodynamics, i.e., the total amount of heat produced or consumed. This amount is determined by the amount of reactive mixture and the extent of deviation from equilibrium; it does not depend on the kinetics of the process.

To determine the enthalpy of the reaction we first derive a differential relation between G and H . For a pure substance,

$$(34) \quad H = G + TS = G - T \left(\frac{\partial G}{\partial T} \right)_{p,N} = \frac{\partial[(1/T)G]}{\partial(1/T)} = \frac{\partial(G/T)}{\partial(1/T)}$$

where we used that $d(1/T)/d(1/T) = 1$ and $-T^2(dG/dT) = \frac{dG}{-\frac{1}{T^2}dT} = dG/d(1/T)$. We also assume that pressure and particle number remain constant.

The same relation holds for the enthalpy and Gibbs energy per mole, as can be seen by dividing out the above equation by number of moles:

$$(35) \quad h_i = \frac{\partial(\mu_i/T)}{\partial(1/T)}$$

where we have added the label i to allow us to write this equation for different species and remembered that the chemical potential is the Gibbs energy per mole.

Let us define the reaction enthalpy analogously to the reaction Gibbs energy

$$\Delta_r H \equiv \sum_{i=1}^M \nu_i h_i \quad (36)$$

Multiplying the Eq. 35 by ν_i and summing over the species, $i = 1 \dots M$, yields

$$\sum_i^M \nu_i h_i = \frac{\partial(\sum_i^M \nu_i \mu_i / T)}{\partial(1/T)} \quad (37)$$

thus yielding

$$\Delta_r H = \frac{\partial(\Delta_r G / T)}{\partial(1/T)} \quad (38)$$

where, again, the pressure and particle number for each species is held constant, and we used the definition of the reaction Gibbs energy 14. On the other hand, according to Eq. 31, the standard Gibbs energy

$$\Delta_r G^\ominus / T = -R \ln K \quad (39)$$

is a pressure independent quantity and does not depend on the particle number either. Thus we obtain that the standard reaction enthalpy obeys the following equation:

$$\Delta_r H^\ominus = -R \frac{d \ln K}{d(1/T)} \quad (40)$$

where we were able to replace the partial derivative w.r.t. T with the full derivative since T is the *only* variable. This equation—which is often referred to as the van't Hoff equation—is particularly useful when the reaction enthalpy happens to be temperature independent or nearly so. Indeed, under these circumstances, the equation above implies the dependence of $\ln K$ on the inverse temperature is simply a straight line:

$$\ln K = -\frac{\Delta_r H^\ominus}{R} \frac{1}{T} + \text{const} \quad (41)$$

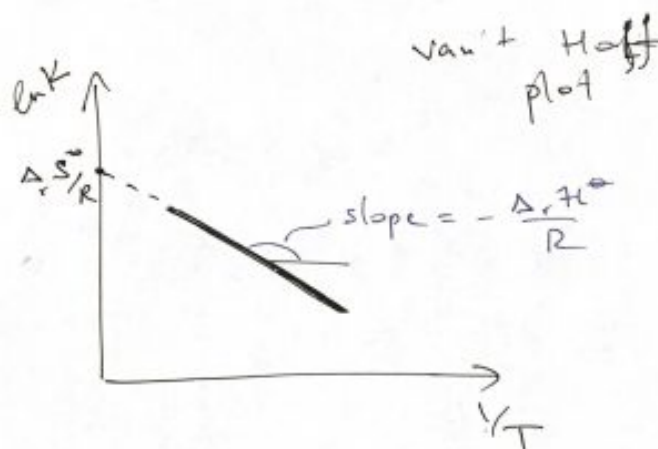
We can fix the constant by defining the reaction's entropy:

$$\Delta_r S \equiv \sum_{i=1}^M \nu_i s_i \quad (42)$$

(s_i stands for the molar entropy of component i) and using the general formula that $G = H - TS$, which, then, implies $\Delta_r G = \Delta_r H - T \Delta_r S$. This and the usual $\ln K = -RT \Delta_r G^\ominus$ yield

$$\ln K = -\frac{\Delta_r H^\ominus}{R} \frac{1}{T} + \frac{\Delta_r S^\ominus}{R} \quad (43)$$

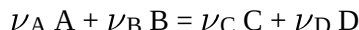
This mathematical statement, which was derived assuming $\Delta_r H$ is temperature independent, automatically implies that the standard reaction entropy is then temperature independent as well. The above equation is quite useful as it allows one to determine both the reaction's enthalpy and entropy by plotting the equilibrium constant as a function of inverse temperature:



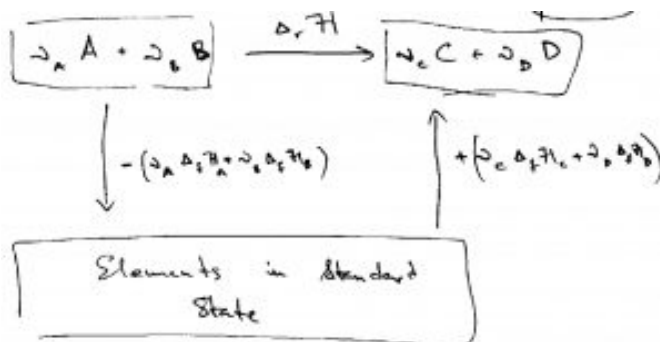
In the above picture, $\Delta_r H > 0$, which formally implies that the reaction is endothermal, i.e., consumes heat. The resulting T -dependence of the equilibrium constant is yet another instance of Le Chatelier's principle: As one attempts to raise the temperature by putting in heat, the equilibrium shifts toward the higher enthalpy state (products in this case) so as to absorb that heat. The converse is also true: Raising the temperature of an exothermal process, $\Delta_r H < 0$, will shift the equilibrium toward the reactants.

Note that in physical terms, $\Delta_r H > 0$ means that, on average, one must break bonds to create the product. On the other hand, heat production, $\Delta_r H < 0$, means the bonds in the molecules comprising the products are stronger than the bonds in the molecules comprising the reactants. This notion underlies the heat production during burning or, more, generally, oxidation of fossil fuels, of course.

Before we attempt a chemical reaction, it is useful to estimate beforehand both the reaction's Gibbs energy and enthalpy, as we have already indicated. Making such estimates from scratch is difficult. Approximate estimates are, however, still possible for a huge variety of distinct reactions since the enthalpies of pure components can be—and in many cases have been—measured. Ignoring, then, the affect of mixing of the individual components with each other, we can present the thermodynamic path from the reactant to the product state as one going through some standard state. And so, for instance, for a reaction:



this mental construction looks something like this:



This is as if one decided to travel from city X (our reactants) to city Y (our products) not directly, but through some city Z (the standard state). Clearly, if one knows the elevation of city X relative to city Z, $h_X - h_Z$, and the elevation of city Y relative to city Z, $h_Y - h_Z$, one can compute the elevation of Y relative to X: $(h_Y - h_Z) - (h_X - h_Z) = h_Y - h_X$. By exactly the same token, the enthalpy is a state function and so the enthalpy difference between two states depends on the identity of those states irrespective of the path one uses to go between the states. The enthalpy of the standard-state to the product-state process is given by $(\nu_C \Delta_f H_C + \nu_D \Delta_f H_D)$, where we used the subscript f to signify “formation”. Likewise, the enthalpy of the standard-state to the reactant-state process is given by $(\nu_A \Delta_f H_A + \nu_B \Delta_f H_B)$. Therefore the enthalpy of the reactant \rightarrow product process is equal to the enthalpy of the reactant \rightarrow standard-state \rightarrow product process:

$$(44) \quad \Delta_r H = (\nu_C \Delta_f H_C + \nu_D \Delta_f H_D) - (\nu_A \Delta_f H_A + \nu_B \Delta_f H_B)$$

where the minus sign reflects that the reactant \rightarrow standard-state leg is in the opposite direction of actually bringing the constituent elements from the standard state to the reactants state. Note that the formation enthalpies $\Delta_f H$ are usually given per mole. This is distinct from the convention adopted in this Course whereby we have attempted to consistently denote quantities per particle or per mole using low-case letters.

Because the Gibbs energy and the entropy are state functions, one can write down equations for the reaction's Gibbs energy and the reaction's entropy that are entirely analogous to the equation above.

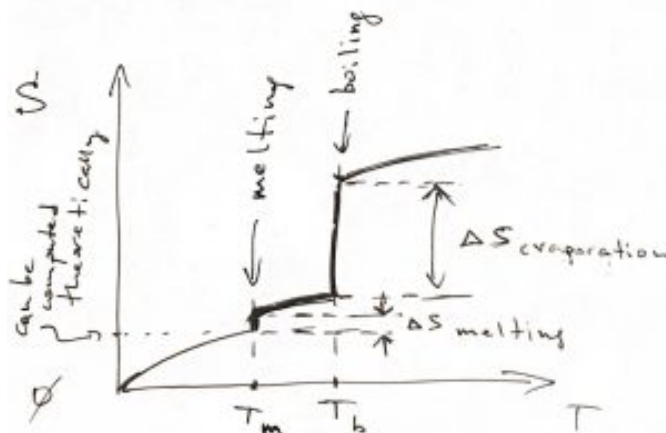
Actual estimates the formation entropy and enthalpy depend on the convention for the standard state. As an example, consider the following procedure: We can use the 3rd Law of Thermodynamics, $S(T = 0) = 0$, to define our reference state. Given this, the entropy at any temperature can be computed by integrating the equation for the heat capacity $C_p = T(\partial S / \partial T)_p$ so long as there is no discontinuous transition takes place:

$$(45) \quad S(T) = S(T = 0) + \int_0^T \frac{c_p}{T} dT = \int_0^T \frac{c_p}{T} dT$$

And, likewise for the enthalpy, where one can integrate the relation $C_p = (\partial H / \partial T)_p$:

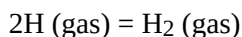
$$(46) \quad H(T) - H(T = 0) = \int_0^T c_p dT$$

If there is, in fact, a phase transition at some temperature, one must add a constant value equal to the transition's entropy at that temperature. Thus the T -dependence of the entropy will look something like this:

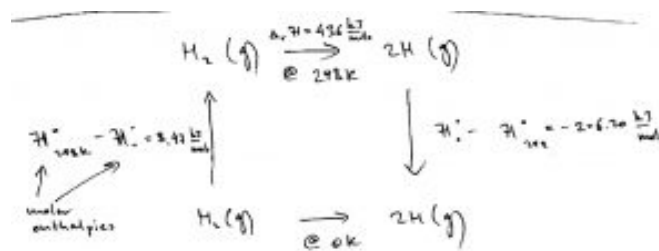


The T -dependence of the enthalpy is qualitatively similar. Consequently, one can compute the Gibbs energy $G = H - TS$, which, recall, is a continuous function of temperature. In practice, it is often most straightforward to actually *compute* the heat capacity of solids, while the heat capacity in the liquid and vapor state is often easier to measure, as are the heats of melting and boiling.

The fact of the enthalpy being a state function allows one to straightforwardly to evaluate the enthalpy at condition other than those readily accessible in the lab. For instance the enthalpy of the reaction



at $T = 0\text{K}$ can be estimated using the measured enthalpy of the reaction at a more accessible temperature using the following construction:



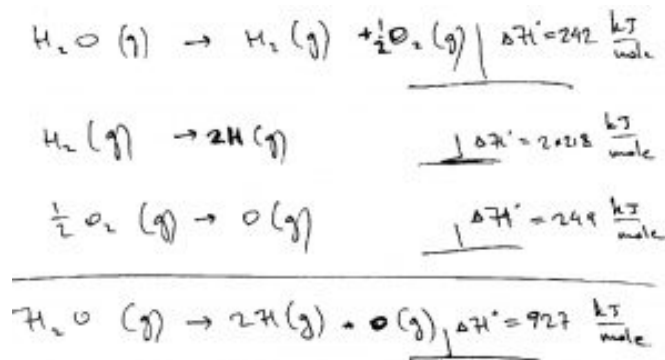
One, then, finds straightforwardly

$$(47) \quad \Delta_r H(T = 0\text{K}) = (8.47 + 436 - 12.4) \text{ kJ/mole} = 432 \text{ kJ/mole}$$

The $T = 0\text{K}$ estimate is not as arcane as one may seem because it can be directly compared with the output of quantum-chemical calculation, which produce most accurate results for the ground state of the system.

The above example is also revealing in the following sense: It illustrates just how much more enthalpy is “stored” in a chemical bond compared with a physical process such as heating or cooling. The enthalpy of the latter processes is clearly comparable to the thermal energy RT , which, then, brings about another important point. The thermal energy scale RT , in gases, is also comparable to the quantity pV_m , where V_m is the molar volume. On the other hand, the energy and enthalpy are related through the equation $H = E + pV$. Thus we conclude that the energy and enthalpy of a chemical bond are numerically close. This should have been expected: Bonding energies are of order several eV, while the thermal scale, $k_B T$, at room temperature is about 1/40 eV. These are useful notions since quantum-chemical calculations actually produce the energy of the bond, while the experiment produces the bond’s enthalpy. Thus equating the two is, generally, an approximation, albeit a good one.

As another illustration of how one can exploit the fact of the enthalpy being a state function, we can determine the enthalpy of the H-O bond, per bond, in a water molecule:



Note the actual strength of the H-OH bond and the H-O bond are not the same, the latter being significantly stronger than the former.

Our final remarks concern the *kinetics* of chemical processes. The thermodynamic considerations above do not directly address the issue of how *fast* the chemical processes in question will actually occur. This should have been clear already because nowhere in the discussion have we even mentioned the mass of the species. But we know that the mass is of decisive importance for how fast molecules move about, given that the typical energy scale for their motion is fixed by the temperature. What thermodynamics *can* do is tell us about the *relative* rates of processes in equilibrium. And so, for instance, we have written the relation between the equilibrium constant and the reaction’s Gibbs energy:

$$(48) \quad K = e^{-\Delta_r G^\ominus / RT}$$

As already mentioned, the equilibrium constant should be thought of as the probability of being in the product state relative to the probability of being in the reactant state. On the other hand, this probability must be equal to the ratio of the rates $\frac{k_{\text{reactants} \rightarrow \text{products}}}{k_{\text{products} \rightarrow \text{reactants}}}$. Indeed, the probability of being in a state is proportional to the flux of the particles toward that state. Thus we obtain an example of what one calls **the detailed balance**:

$$(49) \quad \frac{k_{\text{reactants} \rightarrow \text{products}}}{k_{\text{products} \rightarrow \text{reactants}}} = e^{-\Delta_r G^\ominus / RT}$$

which essentially states that in equilibrium, the ratio of the transition rates between two states must match the free energy difference between the two states. We have already encountered a simpler version of the above statement, i.e., that the rates of transfer between two *microstates* 1 and 2 must obey the following relation:

$$(50) \quad \frac{k_{1 \rightarrow 2}}{k_{2 \rightarrow 1}} = e^{-(E_2 - E_1) / k_B T}$$

Again, these relations do not tell us anything about the absolute values of the rate constants, only their ratios. The absolute values of rates contain time units. In order to obtain a quantity of units time from a quantity of units energy, one must use a quantity of units mass. The actual way to do this depends on the amount of quantum effects, to which we turn next.

II

Quantum Mechanics

11.

Foundations of Quantum Mechanics. Operators. Wave function. The Schrodinger Equation.

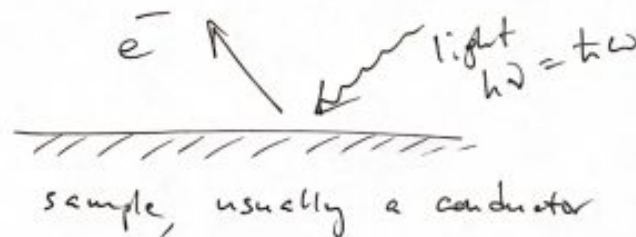
By the end of the 19th century, mathematical physicists became very good at solving Newton's equations of motion for particles and the equations of motion for waves, such as light waves or sound waves, due to D'Alembert, Euler, and others. So advanced was the state of mathematics that some proclaimed soon there would be no open physical questions to solve. Indeed, the physical models and much of the mathematics we still use to describe electromagnetic, gravitational, acoustic, and thermal phenomena, among others, were developed already in the 19th century. At the same time, experimenters were rapidly improving their methods, too, thus becoming able to study physical phenomena at progressively smaller length scales and shorter times scales. And that is when it became clear that something is missing in the classical description. Those open questions are too many to list here. We will limit ourselves to only a few. Some of these questions we will be able to address in a qualitative fashion.

1. Perhaps of most importance for Chemistry and Biology is the following question: How is it possible for bound states, such as atoms, molecules, or solids to exist? Electrons are known to be negatively charged and atomic nuclei to be positively charged. According to Earnshaw's Theorem (1842), a set of electrical charges is unstable. Yet somehow electrons manage to stick around atomic nuclei, seemingly forever, without falling on the nuclei. The resulting finite size of atoms underlies the very notion of a particle and the notion of matter itself. Furthermore, if one takes the classical perspective that electrons spin around the nucleus, they must emit radiation because their motion is constantly accelerating toward the nucleus, because of the Coulomb attraction between the two charges. Indeed, the only way for an accelerating/decelerating charge to exchange the energy with the rest of the world is to emit/absorb radiation; this is how radio transmitters and synchrotrons actually work. Following this continuous loss of energy, the electrons must eventually fall on the nucleus. Yet they do not, nor is there any radiation emitted by atoms or molecules in their lowest-energy state. (Note bodies that spin around each other owing to the mutual gravitational pull do emit gravity waves, which eventually leads to their collision.)
2. Classical Physics implies that the energy of an electron spinning around a nucleus can take arbitrary (negative) values, yet the absorption spectra of gases indicate that the energy of the electron changes in discrete bits. For instance, the energy of a hydrogen atom can have any of the following values: $E_n = -\text{const}/n^2$, where $n = 0, 1, 2, \dots$. In addition to its basic significance, this notion underlies the field of spectroscopy, which is arguably the most important experimental tool of natural sciences.
3. Classical Physics does not offer a way to approach the fundamental question of whether there is a smallest indivisible unit of matter, thus creating a difficult conceptual problem.
4. Why are there seemingly two, seeming distinct ways for energy to travel through space, that is, in terms of compact particles and in terms of waves? Furthermore, these two distinct ways are actually not mutually exclusive for massive particles, and is made clear from the interference patterns created by electronic beams. https://en.wikipedia.org/wiki/Electron_diffraction
5. One of the worst problems for Classical Physics is the photoelectric effect. Hereby, a solid exposed to light with a wavelength shorter than a certain threshold value emits electrons. Surprisingly, the energy

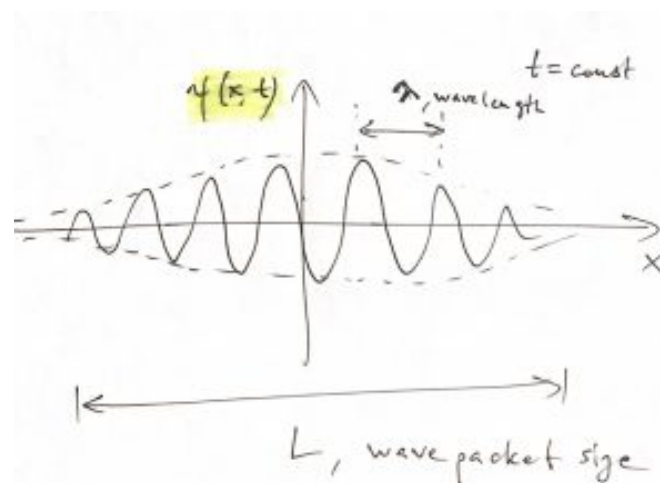
of an individual electron does not increase with the light's intensity, but depends only on the light's frequency ν , according to the following formula:

$$(1) E_{\text{electron}} = h\nu - W$$

The quantity W is called the work function. No electrons are emitted for $\nu < W/h$. Classically, nothing prevents a material from ejecting an electron once some requisite amount of energy is absorbed. The energy can be delivered using light of any frequency, including those less than W/h , subject to the intensity and exposure time, of course. Nor is there a constraint on the relation between the energy of the ejected electron and the light's frequency. In contradistinction with these expectations, there seems to be a smallest amount—or “quantum”—of energy that can be absorbed by the sample per absorption event. (In practice, photoelectric spectroscopy is usually done on conducting samples so that the negative charge can be replenished. Non-conductive samples quickly become positively charge which increases the work function over time.) In fact, this quantum of energy is equal to $h\nu$, while the work function W , then, represents the smallest value of the binding energy of the electron in the solid.

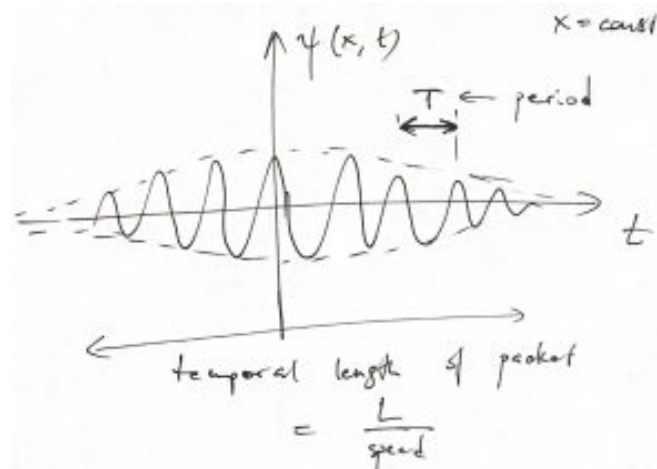


Quantum Mechanics has successfully resolved those and many more issues; it is regarded as one of the most successful microscopic descriptions. From the mathematical perspective, the main object of this description is the *wave packet*, which is function of both space and time. At a specific value of time, it is a function of the coordinate only, as we show below:



We see that the notion of a wave packet combines the notions of a wave and a particle: The spatial extent L of the packet can be regarded as the particle size. Indeed, so long as the spatial resolution of our experiment is greater than L , the internal, “wavy” structure of the packet won’t even be detected. On the other hand, the oscillations within the packet can be regarded as wave-like, oscillatory motions and would be detectable given sufficient spatial resolution. Because at any given moment in time, a wave-packet is a function of the coordinate, call it $\psi(x)$, it technically corresponds to an infinite number of degrees of freedom, one per each space-point x . This drastically complicates the mathematics of the theory. In comparison, to describe the state of motion of a solid object in 3D, we only need to specify the location of its center of mass, its orientation, and the velocities of its translational and rotational motion, which, in total, is 12 variable at most.

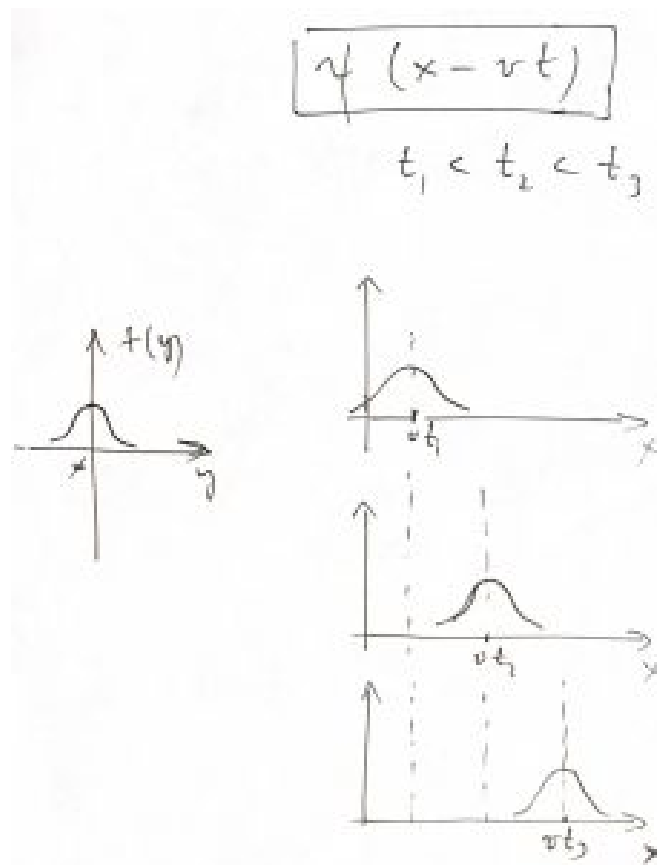
If the wave packet moves in space as some non-zero speed, its locality in space also implies a locality in time:



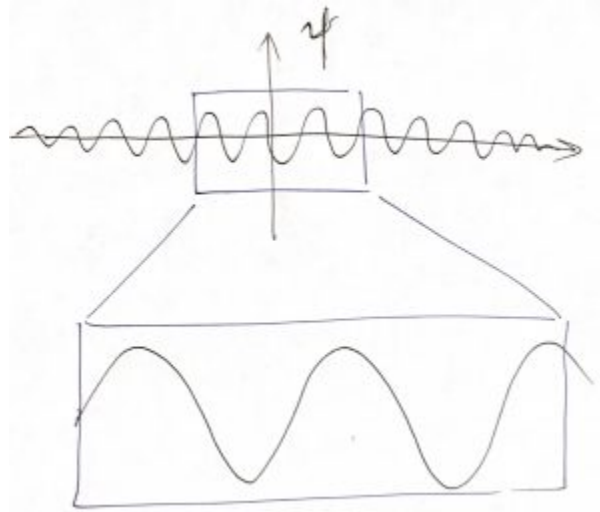
We, then, interpret the non-zero portion of the time dependence of the signal as the moment where our “particle-wave” passes through the point x . From now on, we focus on wave packets in 1D that move to the right or the left without changing their shape. While not too constraining for our purposes here, this simplifies the algebra since now the coordinate and time enter our wave packet in a particular combination:

$$(2) \quad \psi(x, t) = f(x - vt)$$

where f is some function. The figure below illustrates the time evolution of the packet, where we used a bell-shaped function f for clarity. (Such rudimentary wave packets are allowed, but are hardly waves in the regular sense of the word.):



To develop a mathematical description for wave packets, we first “zoom in” on the central portion, which looks like a plane wave:



Let us for now focus exclusively on *plane waves*: Consider a cosine profile with an arbitrary amplitude A and phase shift φ_0 :

$$\begin{aligned}
 f(y) &= A \cos\left(\frac{2\pi}{\lambda}y + \varphi_0\right) \\
 &= A \left[\cos\left(\frac{2\pi}{\lambda}y\right) \cos(\varphi_0) - \sin\left(\frac{2\pi}{\lambda}y\right) \sin(\varphi_0) \right] \\
 &\equiv C_1 \cos\left(\frac{2\pi}{\lambda}y\right) + C_2 \sin\left(\frac{2\pi}{\lambda}y\right)
 \end{aligned}
 \tag{3}$$

where $C_1 \equiv A_1 \cos(\phi_0)$, $C_2 \equiv -A_1 \sin(\phi_0)$, and we used the trigonometric formula $\cos(x + y) = \cos(x) \cos(y) - \sin(x) \sin(y)$ to derive the last equality. The latter equality demonstrates that any linear combination of \cos and \sin waves with the same period can be presented as a cosine wave with a phase shift. (It can be presented as a sine wave, as well, of course.) Note the denominator λ was needed so that the argument of the cosine is dimensionless, while the factor 2π is introduced simply for convenience so that the function is periodic with period λ . (Recall that the functions $\cos x$ and $\sin x$ are periodic with period 2π .) The quantity λ is called the wavelength, which it really is. It is convenient to introduce a new quantity called the wave vector:

$$k \equiv \frac{2\pi}{\lambda} \tag{4}$$

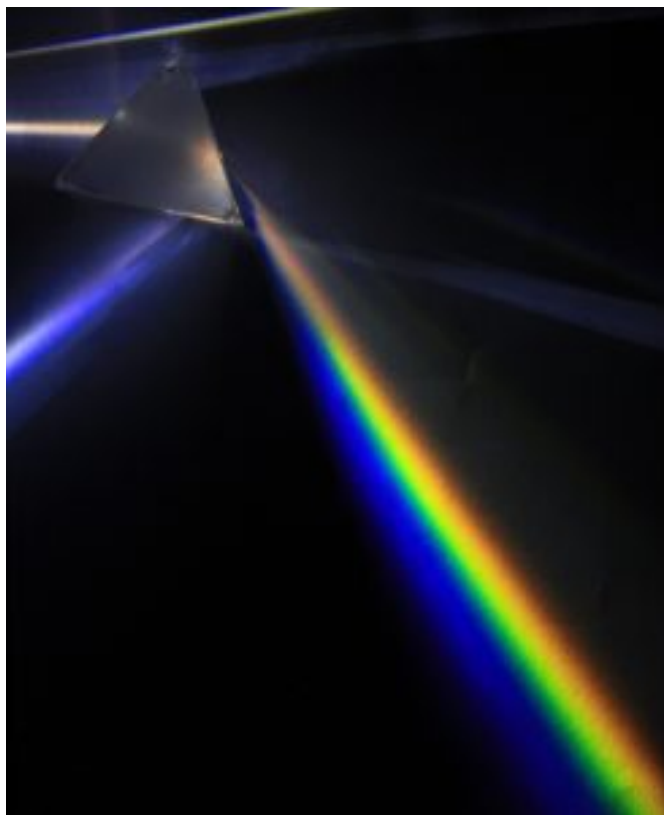
The resulting plane wave is, then,

$$\psi_{\text{mc}}(x, t) = A \cos[k(x - vt) + \varphi_0] \equiv C_1 \cos(kx - \omega t) + C_2 \sin(kx - \omega t) \tag{5}$$

where we have introduced yet another quantity, called the circular (or angular, or cyclic) frequency:

$$\omega \equiv k v = 2\pi \frac{v}{\lambda} = \frac{2\pi}{T} = 2\pi \nu \tag{6}$$

since the wavelength is the distance traveled by the wave in one period of the oscillation, $\lambda = vT$, while the regular frequency, $\nu = 1/T$, is simply the number of oscillations per unit time; there is exactly one oscillation per period of the wave. We used the subscript “mc” in Eq. 5 to signify “mono-chromatic”, since our signal is characterized by a single oscillation frequency. There is one-to-one correspondence between the frequency of light waves and their color (Image: [D-Kuru](#), CC BY-SA 3.0 AT, via Wikimedia Commons):



The circular frequency ω is more convenient than the standard frequency ν because we don't have to drag along the 2π factor, and so we shall use exclusively ω , not ν , while calling is simply *the frequency*. In this notation, the energy of light quantum becomes:

$$(7) \quad h \nu = \frac{h}{2\pi} \pi \nu \equiv \hbar \omega$$

where \hbar (pronounced 'h-bar') is a version of Planck's constant:

$$(8) \quad \hbar \approx 1.05 \cdot 10^{-34} \text{ J sec}$$

Though used frequently for practical applications, the constant \hbar is of no fundamental significance; it is simply a means of converting between frequency and energy scales, similarly to how the Boltzmann constant is a means of converting between Joules and Kelvins. This said, the central notion of the correspondence between frequency and energy:

$$(9) \quad E = \hbar \omega$$

is not at all obvious, although it is natural for many reasons some of which will become clearer in due time. Here we take the correspondence between the frequency of a cyclic motion and its energy—which is at the very heart of Quantum Mechanics—as an experimental fact implied by the photoelectric effect.

Our next task to establish how we can describe the dynamics of inertial objects using operations that can be applied to waves. (This is a non-trivial task because excitations that we know are wave-like, such as light or sound, are actually massless!) Specifically, we know that the energy E of an inertial object is given the expression

$$(10) \quad E = \frac{p^2}{2m} + V(x)$$

where p is the momentum. The potential energy $V(x)$ is something that is there irrespective of whether the wavepacket is present or not. Thus we only need to determine a mathematical operation to extract the energy and momentum from the functional form of a wave packet.

First we tackle the total energy and take advantage of the simple linear connection [9](#) between the frequency and energy. What is the mathematical operation that would allow us to extract the frequency ω ? We notice that for

the monochromatic wave signal from Eq. 5, differentiating twice w.r.t. to time produces the same wave signal, but multiplied by $(-\omega^2)$:

$$(11) \quad \frac{\partial^2}{\partial t^2} \psi_{\text{mc}} = -\omega^2 A \cos[k(x - vt) + \varphi_0] = -\omega^2 \psi_{\text{mc}}$$

Thus we establish that there is, in fact, a mathematical operation that extracts the frequency squared:

$$(12) \quad -\frac{\frac{\partial^2}{\partial t^2} \psi_{\text{mc}}}{\psi_{\text{mc}}} = \omega^2$$

Mathematical situations exemplified by Eq. 11, where an application of a mathematical operation— or **operator**—to a function produces the very same function times a fixed number are of significance to us. Generally, we say that if some operator \hat{O} , when applied to a function, produces the very same function times a *fixed* number:

$$(13) \quad \hat{O} f = \lambda f$$

we call the function f an eigenfunction of the operator \hat{O} , where the number λ is the corresponding eigenvalue. Arguably the simplest operator is when one simply multiplies a function by a constant:

$$(14) \quad \hat{O} \equiv C$$

Since $C f(x) = C f(x)$ for any function f , this means that every function is a eigenfunction of the multiplication operator, where the multiplier itself is the corresponding eigenvalue. A less trivial example is the operation of differentiation:

$$(15) \quad \hat{O} \equiv \frac{\partial}{\partial x}$$

To determine the eigenfunction, if any, of this operator we must solve a differential equation, as seen by substituting the above equation into Eq. 13:

$$(16) \quad \frac{\partial}{\partial x} f = \lambda f$$

This is, of course, a very familiar differential equation that is solved by the exponential function

$$(17) \quad f(x) = A e^{\lambda x}$$

where A is an arbitrary constant. This is a general pattern for linear operators:

$$(18) \quad \hat{O} A f = A \hat{O} f$$

If a function is an eigenfunction of a linear operator, then multiplying this function by an arbitrary constant also produces an eigenfunction. This embarrassment of riches, so to speak, is never a problem, since we usually end up normalizing our eigenfunction as appropriate to the task at hand. This does bring about an important point that we are generally interested in eigenfunctions that are normalizable, to be discussed in more detail a bit later. In the rest of the class, we will focus exclusively on linear operators.

To give one more example of a linear operator, consider this:

$$(19) \quad \hat{O} \equiv x \frac{\partial}{\partial x}$$

It is not difficult to see that this operator has the power law function as its eigenfunction

$$(20) \quad f(x) = A x^n$$

where n is the corresponding eigenvalue and A is an arbitrary constant. This is because $x \frac{d}{dx} A x^n = A x n x^{n-1} = n A x^n$.

Let us return to the search for a linear operator that would extract ω . Simply taking a square root from Eq. 12 won't do us much good since the operation $\sqrt{\hat{O} f}$ produces a quantity going as $f^{1/2}$, which is generally

not equal to f times a constant. One might think that differentiation once w.r.t. t would do the trick since it brings down a factor of ω , but, according to Eqs. 15 through 17, the corresponding eigenfunction would be an exponential function $e^{\omega t}$, not an oscillatory function we need to describe a wave. Undeterred, we go ahead and apply the $\frac{\partial}{\partial t}$ operator to the function 5

$$(21) \quad \frac{\partial}{\partial t} [C_1 \cos(kx - \omega t) + C_2 \sin(kx - \omega t)] = \omega C_1 \sin(kx - \omega t) - \omega C_2 \cos(kx - \omega t)$$

and ask whether this can be made equal to $\lambda [C_1 \cos(kx - \omega t) + C_2 \sin(kx - \omega t)]$, where λ , then, would be the eigenvalue. Equating this to the r.h.s. of Eq. 21 yields

$$\lambda C_1 = \omega C_2$$

$$(22) \quad \lambda C_2 = -\omega C_1$$

This system of equations has an infinite number of solutions. After dividing the top equation by the bottom equation, one observes that for each of those solutions, however, it must be true that

$$(23) \quad C_1^2 = -C_2^2$$

This implies that one of the numbers C_1 and C_2 must be the square root of a negative number! Although disconcerting at first, this seemingly absurd idea shouldn't be discarded quite yet. To give an historical example, the ancients couldn't accept for the longest time the concept of a negative number, and whenever negative numbers appeared in calculations as intermediate results they simply thought of those as being "owed". For instance the operation $2 + 3$ makes perfect sense, but the equivalent operation $2 + 3 = 2 + (8 - 5) = 2 - 5 + 8 = -3 + 8$ involves a negative number as an intermediate result. One may think of this -3 number as a result of owing somebody 3 dollars while physically having 8 dollars on hand, and so the effective total is still positive and everything is fine. For instance, suppose you have \$1,000, which you can spend as you please, but, at the same time, you owe your bank \$1,500. In effect, your total assets are actually negative: $-\$500$. Yet both you and the bank have positive amounts of money, and so there is no need to use negative numbers so long as we are willing to use the concept of debt. Yet for the efficiency of mathematical computation, it is easier to simply use negative numbers.

By the same token, let us generalize the concept of multiplication by allowing the square of a number to be negative in an intermediate calculation, so long as the *final* result does not involve such "aberrant" numbers. For concreteness, we set

$$C_1 = 1$$

$$(24) \quad C_2 = i$$

where we define a new quantity i , called the "imaginary" unit:

$$(25) \quad i^2 = -1$$

So long as our final answer does not involve i , we should regard it simply as a convenient computational tool, no more no less. Again, on a historical note, the imaginary unit appeared as an intermediate result already centuries ago, during ancient calculations of the roots of polynomial equations, sometimes even when the roots themselves were "normal" numbers whose squares were non-negative.

Thus we obtain

$$(26) \quad \begin{aligned} \frac{\partial}{\partial t} [\cos(kx - \omega t) + i \sin(kx - \omega t)] &= \omega \sin(kx - \omega t) - i \omega \cos(kx - \omega t) \\ &= -i\omega [\cos(kx - \omega t) + i \sin(kx - \omega t)] \end{aligned}$$

i.e. the function $\cos(kx - \omega t) + i \sin(kx - \omega t)$ is an eigenfunction of the operator $\frac{\partial}{\partial t}$ with the corresponding eigenvalue $(-i\omega)$. Likewise, one can show that

$$(27) \quad \frac{\partial}{\partial x}(\cos x + i \sin x) = i(\cos x + i \sin x)$$

Comparing this with Eqs. 15—17 shows that

$$(28) \quad e^{ix} = \cos x + i \sin x$$

which is the celebrated Euler's formula. Expanding the exponential in the left hand side in the Taylor series yields

$$(29) \quad \begin{aligned} e^{ix} = \sum_{n=0}^{\infty} \frac{(i)^n x^n}{n!} &= \sum_{n=0}^{\infty} \frac{(i)^{2n} x^{2n}}{(2n)!} + \sum_{n=0}^{\infty} \frac{(i)^{2n+1} x^{2n+1}}{(2n+1)!} \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{(2n)!} + i \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)!} \end{aligned}$$

where we broke up the original sum into the sums over the even and odd powers of x and used that $i^{2n} = (i^2)^n = (-1)^n$. We recognize the two sums on the r.h.s. as the Taylor expansions for the cosine and sine functions, respectively, consistent with the Euler formula. (Neither of these two expansions contains the imaginary unit!) Hence, the imaginary unit i is simply a clever bookkeeping device that allows us to simultaneously work with two numbers at a time. Such “compound” numbers, each of which is simply a pair of actual numbers, say x and y , are called complex numbers and are written as this

$$(30) \quad z = x + i y = i y + x$$

where x is called the real part and y is called the imaginary part, for historical reasons. The two numbers x and y are equally important, and there is nothing more real about the x than the y .

Now, for two complex numbers $z_1 = x_1 + i y_1$ and $z_2 = x_2 + i y_2$,

$$(31) \quad z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$$

where we observe that one can add two pairs of number in one shot by using complex numbers. A more interesting example is that where multiply two complex numbers:

$$(32) \quad \begin{aligned} z_1 z_2 &= (x_1 + i y_1)(x_2 + i y_2) = x_1 x_2 + i^2 y_1 y_2 + i(x_1 y_2 + x_2 y_1) \\ &= x_1 x_2 - y_1 y_2 + i(x_1 y_2 + x_2 y_1) \end{aligned}$$

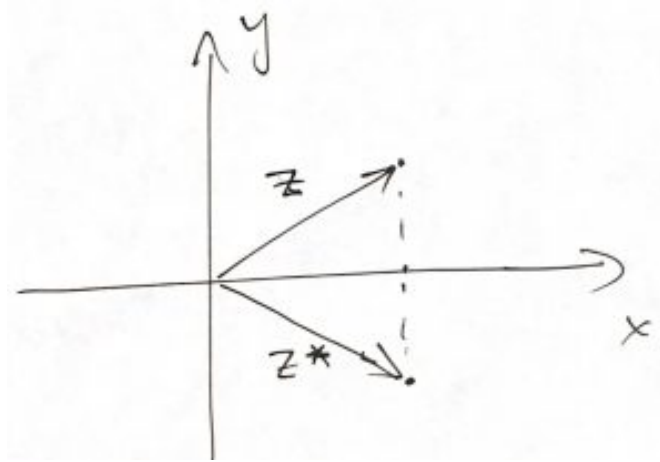
If we further substitute $x_1 = x_2 = x$ and $y_1 = -y_2 = y$ into the above equation, we obtain

$$(33) \quad z^* z = x^2 + y^2$$

where we have introduced the complex conjugate of the number $z = x + i y$:

$$(34) \quad z^* = x - i y$$

The complex number z and its complex conjugate z^* , when pictured on the (x, y) plane, are mirror images of the other w.r.t. to the horizontal axis:



Because $x^2 + y^2$ is the length square of the vector whose endpoint is the location of the complex number z , one customarily uses the following notation:

$$(35) \quad z^* z \equiv |z|^2$$

Now, according to Eq. 26, the eigenvalue of the operator $\frac{\partial}{\partial t}$ is $-i\omega$. Since $i\hbar \times (-i\omega) = \hbar\omega$, we conclude the energy operator is given by:

$$(36) \quad \hat{H} = i\hbar \frac{\partial}{\partial t}$$

To extract the momentum of a wave, we use Einstein's result on the connection between the energy and momentum that applies for both massive and mass-less objects:

$$(37) \quad E^2 = p^2 c^2 + (m_0 c^2)^2$$

where p is the momentum, c is the speed of light, and m_0 is the rest mass, i.e., the mass in the frame moving with the object. For a mass-less object, such as a particle of light, $m_0 = 0$, and so

$$(38) \quad E = pc$$

while $E = \hbar\omega$. Thus,

$$(39) \quad p = \hbar \frac{\omega}{c} = \hbar \frac{2\pi\nu}{c} = \hbar \frac{2\pi}{\lambda} = \hbar k$$

where $k = \frac{2\pi}{\lambda}$ is called the wave vector.

Since

$$(40) \quad \frac{\partial}{\partial x} e^{i(kx - \omega t)} = i k e^{i(kx - \omega t)}$$

we conclude that the momentum operator is simply the derivative w.r.t. to the coordinate times $(-i\hbar)$:

$$(41) \quad \hat{p} = -i\hbar \frac{\partial}{\partial x}$$

The kinetic energy operator, then, is given by

$$(42) \quad \frac{\hat{p}^2}{2m} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right) \left(-i\hbar \frac{\partial}{\partial x} \right) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Now we take the classical expression for the total energy $E = \frac{p^2}{2m} + V(x)$ and plug in it the quantum-mechanical values for E and p :

$$(43) \quad \frac{i\hbar \frac{\partial}{\partial t} \psi}{\psi} = \frac{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi}{\psi} + V(x)$$

After multiplying through by ψ we obtain the celebrated **Schrodinger Equation**:

$$(44) \quad i\hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x) \psi(x, t)$$

where we have explicitly indicated that the function $\psi(x, t)$, which solves this equation, depends both on the time and coordinate. Accordingly, the above equation is sometimes called the time-dependent Schrodinger equation. Any solution of a Schrodinger equation are usually called a **wave-function**, for historical reasons.

Time dependent equations such as Eq. 44 are hard to solve. Fortunately, we are mostly interested here in solutions corresponding to *bound* states, which are stationary, i.e., time independent. To see how such solutions arise, we substitute the following functional form in Eq. 43

$$(45) \quad \psi(x, t) = X(x) T(t)$$

i.e., we have presented the full wave-function as a product of a function that depends exclusively on the coordinate and a function that depends exclusively on time. This method of solving differential equations for functions of more than one variable is called “separation of variables”. We thus obtain

$$(46) \quad \frac{i\hbar \frac{\partial}{\partial t} \cdot T(t)}{T(t)} = \frac{[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)] \cdot X(x)}{X(x)}$$

We observe that the l.h.s. depends exclusively on time, while the r.h.s. exclusively depends on the coordinate. But the time and coordinate are independent quantities, and so the above equation is meaningful when both sides are constants that are independent of x and t :

$$(47) \quad \frac{i\hbar \frac{\partial}{\partial t} T(t)}{T(t)} = \text{const}$$

$$(48) \quad \frac{[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)] \cdot X(x)}{X(x)} = \text{const}$$

where the constant is the same in both equations. We now re-write Eq. 49 this way

$$(49) \quad i\hbar \frac{\partial}{\partial t} \cdot T(t) = \text{const} T(t)$$

while remembering that the operator on the l.h.s. is the energy operator. Thus the time dependent part of the variable-separated solution from Eq. 45 is an eigen-function of the energy operator, whose eigenvalue is, of course, the energy itself and is, by construction, a time-independent quantity:

$$(50) \quad \text{const} = E$$

Thus those variable-separated solutions are, in fact, energy conserving solutions. The value E itself of the total energy is of yet unknown, unfortunately. The above equation can be however substituted into Eq. 48 to obtain the following equation:

$$(51) \quad \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] X(x) = E X(x)$$

which is called the time-independent Schrodinger Equation, or, often, simply the Schrodinger Equation. Note we have replaced the partial derivative w.r.t. x by the full derivative because the function X depends only on x .

Thus we observe that the task of determining the possible values of the energy of our system reduces to finding all possible eigenfunctions and eigenvalues of the operator on the left. This operator:

$$(52) \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

is called the Hamiltonian operator. It depends exclusively on the coordinate and not on time. For each eigenvalue so found, one can immediately solve for the time-dependent part since now the constant in Eq. 49 is known:

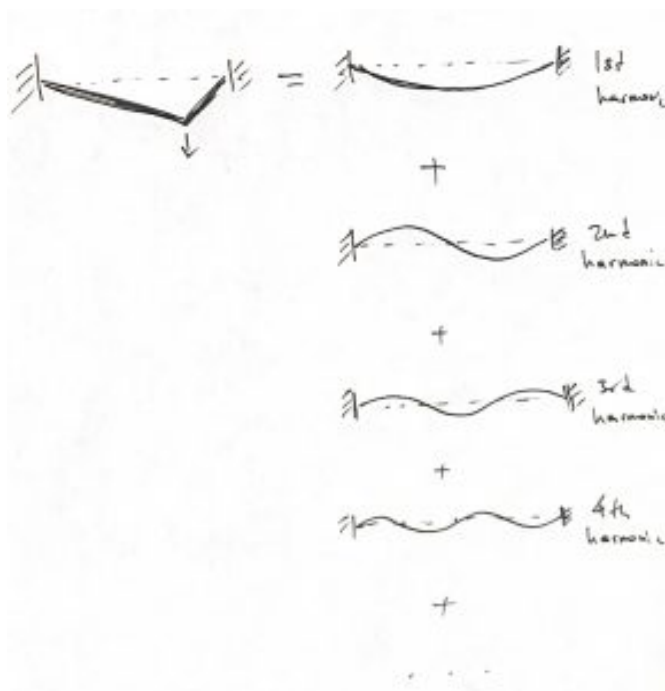
$$(53) \quad i\hbar \frac{\partial}{\partial t} T(t) = E T(t) \Rightarrow T(t) = C e^{-iET/\hbar}$$

where C is a constant. If we are fortunate enough to be able to determine all possible eigenfunctions and corresponding eigenvalues, then the solution to the full, time-dependent problem from Eq. 44 is a linear combination of those solutions:

$$(54) \quad \begin{aligned} \psi(x, t) &= \sum_j T_j(t) X_j(x) \\ &= \sum_j C_j e^{-\frac{iE_j t}{\hbar}} \psi_j(x) \end{aligned}$$

where we use the label j to denote distinct eigenfunctions. The above formula utilizes the notion that if each of two distinct functions solves a linear equation—Eq. 44 in this case—then their sum does, too.

The distinct eigenfunctions in Eq. 54 correspond to the distinct microstates we have already alluded to many times in the Thermo part of the Course. Now we have a way to actually determine those microstates, at least in principle. The corresponding eigenvalues, E_j , may or may not be numerically different. If the energy eigenvalues for two or more distinct microstates happen to be numerically equal, we refer to that situation as the corresponding energy value being *degenerate*. As we have seen in the Thermo part, one expects that the degeneracy generally grows with E . Since, $e^{-\frac{iE_j t}{\hbar}} = 1$ in the beginning, $t = 0$, the constants C_j must be chosen so that $\psi(x, t = 0)$ matches the initial conditions of interest. For instance, imagine plucking a guitar string like on the l.h.s. below:



The r.h.s. of the picture exemplifies the eigenfunctions of the time-independent Schrodinger equation, where the energy eigenvalue increases from top to bottom. We observe that the initial spatial profile of the string resembles the lowest energy wavefunction quite a bit, but other harmonics must be admixed, with some weight, to fully recover that initial spatial profile. Because of this, the overall dynamics of the string will include motions at more than one energy and, hence, frequency. These high frequency motions can actually be heard when a musical instrument is played and are called “harmonics.” Similarly, we will sometimes informally refer to distinct solutions of the time-independent Schrodinger equation as harmonics. The general trend is that higher-order, shorter-wavelength harmonics correspond to higher energy motions. For a string, such higher frequency, higher energy motions mean a higher pitch sound.

Finally, to determine the meaning of the wave function itself, we again use insight from wave mechanics. There we know that the energy density of a wave is proportional to the wave’s amplitude squared. To interpret this from a particulate viewpoint, the energy density is equal to the energy per particle times the particle density. Thus the amplitude-squared is proportional to the particle density. Because our wave function generally consist of two contributions, corresponding to the real and imaginary parts of the wave function, we simply add together the contributions of the two parts. According to Eqs. 33 and 35 the density $p(x)$ of the particles at point x is given by the quantity

$$(55) \quad p(x) = \psi^*(x, t)\psi(x, t) = |\psi(x, t)|^2 = |\psi^*(x, t)|^2$$

The vast majority of textbooks postulates that $p(x)$ is the *probability* to find the particle(s) at location x . While practical, this interpretation is misleading. That a quantity is distributed—and $p(x)$ certainly varies in space and time, in most cases—does not necessarily mean that the quantity is random. For instance, the digits of the number $\pi = 3.141529 \dots$ may seem to be random—and are, in fact, uniformly distributed!—they are not at all random, but are computed using a specific procedure. Likewise, there is nothing stochastic about the quantum-mechanical equations of motion. (Though they are mightily complicated at times!) An interesting, somewhat advanced discussion of the probabilistic interpretations of Quantum Mechanics can be found at https://getpocket.com/explore/item/how-to-make-sense-of-quantum-physics?utm_source=pocket-newtab. Still, in most cases, we cannot fully control the initial conditions in experiment, and so the notion of $p(x)$ being a distribution of probability becomes quite accurate. As with any distribution, the chances of recovering values of x within an interval $[x_1, x_2]$ are evaluated by integrating the distribution:

$$(56) \quad (\text{probability of } x_1 < x < x_2) = \int_{x_1}^{x_2} p(x) dx = \int_{x_1}^{x_2} |\psi(x, t)|^2 dx$$

In many cases, we are interested in one particle at a time, in which case the total probability to find the particle *somewhere* in space is 1. In such cases, we normalize the wavefunction to unity:

$$(57) \quad \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1$$

Being primed by classical physical, many people struggle with the precise meaning of the quantum mechanical equations of motion and the wavefunction itself. This may explain multiple efforts to interpret quantum mechanics via purely classical means. Some of these of efforts are misguided, but some have resulted in useful ideas. For instance, Eq. 39 suggests that one may associate a wave length to a anything that has a momentum, such as a body moving with some speed v and, hence, possessing momentum $p = mv$. One may formally associate the following quantity of dimensions length to this motion, called **the de Broglie wavelength**:

$$(58) \quad \lambda_{\text{dB}} = \frac{\hbar}{p} = \frac{\hbar}{mv}$$

This yields an informal criterion for the motion of the object of size L being classical:

$$(59) \quad \lambda_{\text{dB}} \ll L$$

A simple estimate shows that the de Broglie wavelength of a macroscopic object becomes incredibly small

even at very very slow speeds. Note that such speeds cannot be any less than their thermal value, i.e., $v_{\text{th}} \sim (k_B T/m)^{1/2}$. By convention we define the thermal de Broglie wave

$$(60) \quad \lambda_{\text{dB, th}} = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}$$

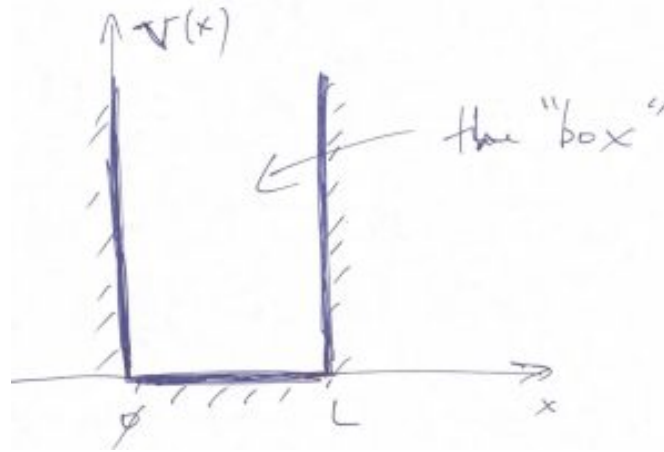
which is simply the expression 58 for the regular de Broglie wavelength with the thermal velocity plugged in, times a constant of order one. Whenever the thermal de Broglie wavelength becomes comparable or greater than the particle size, we can expect quantum effects. For instance, the motions of protons in water are quite quantum-mechanical, which explains the unusually high dielectric susceptibility of water, among other things. For heavier atoms, quantum effects becomes less pronounced. In contrast, the motions of electrons are largely quantum mechanical, which is exceptionally important for bonding as we discuss in the next Chapter.

Bonus discussion: The normalization condition embodied in Eq. 57 partially fixes an aforementioned issue that each operator has an infinite number of equivalent eigenfunctions that differ only by an overall multiplicative number. The fix is not complete since the above equation only fixes the absolute value of the multiplicative constant, which could be either positive or negative or, generally, complex-valued. Remarkably, the seeming mathematical ambiguity has physical consequences, which we won't have a chance to discuss in this Course except for one example, see the next Chapter. In any event, this ambiguity does not arise, if we confine ourselves to considering just one microstate at a time and the wavefunction of the microstate in question has a limited spatial extent. In such cases, one can use ideas from Linear Algebra to show that the solution of the time-independent Schrodinger equation 51 can always to be chosen to be real-valued, i.e., have just one, not the two components that were necessary to define a wave packet. This means, among other things, that every wave packet is wavefunction, but not every wavefunction is a wave-packet. Specifically, wave functions of bound states are not wavepackets. In physical terms, this is because bound states do not correspond to transfer of mass—and energy, momentum, etc.—through space, while wavepackets do transport energy through space. It is quite reasonable, and even beneficial, to think of the wave functions of bound states as standing waves. Indeed, consider an equally weighted sum of a wave propagating rightward and a wave propagating leftward: $\psi(x, t) = \frac{1}{2}[e^{i(kx-\omega t)} + e^{i(-kx-\omega t)}] = e^{-i\omega t} \cos(kx)$. We observe that the coordinate-dependent part of such a wave function can be made purely real-valued, while the corresponding particle density profile $|\psi(x, t)|^2 = \psi^* \psi = e^{+i\omega t} \cos(kx) e^{-i\omega t} \cos(kx) = \cos^2(x)$ has no time dependence, consistent with the microstate being stationary. Thus a standing wave can be thought of as a sum of two waves of equal magnitude that propagate in exactly opposite directions, which, of course, results in no energy transfer. One can easily generate standing waves on the surface of a liquid contained in a vessel of finite size. The radiation inside a working microwave oven is also an example of a standing wave. The wavefunctions of electrons bound inside an atom or a molecule, and the wave functions of the nuclei inside a molecule are all standing waves. The wave function of an atom flying through space is not a standing wave, but, instead, is a wave packet. In the remainder of the Course, we will focus exclusively on bound states.

12.

Bound states. The particle in the box and other quantum-mechanical models. Quantum numbers. Heisenberg's uncertainty principle. Atoms and Bonding.

The understanding of how long-lived bound states come about is, arguably, the most important benefit of Quantum Mechanics. To begin the discussion, we start off with the simplest, even if artificial model, where we place our system in a box with infinite walls. Consider a “particle in the box” or square well with infinity walls, whereby the potential energy vanishes inside the box while being infinitely high outside the box:



$$(1) \quad V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & x \leq 0 \text{ and } x \geq L \end{cases}$$

Let us recap the time-independent Schroedinger Equation below:

$$(2) \quad -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x)$$

To be clear, we are looking for finite energy solutions of the Schrodinger equation, which means the r.h.s. must be finite (i.e. not infinite). Since the l.h.s. is thus also finite, we must have it that the wave function must vanish outside the box. Otherwise, the product $V(x)\psi(x)$ would be infinite. Thus we have $\psi(x) = 0$ for $x \leq 0$ and for $x \geq L$. This fixes the boundary conditions for the values of the wave function at the edges of the box:

$$(3) \quad \psi(0) = 0$$

$$(4) \quad \psi(L) = 0$$

Inside the box, the potential energy vanishes, $V(x) = 0$, therefore we have a very simple equation

$$(5) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x)$$

Our task is to find all allowed values of the energy E . As we saw in the preceding Chapter, the above equation is solved by a linear combination of the sine and cosine function:

$$(6) \quad \psi(x) = C_1 \cos(kx) + C_2 \sin(kx)$$

Inserting this solution in the l.h.s. of Eq. 5 yields

$$(7) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} [C_1 \cos(kx) + C_2 \sin(kx)] = \frac{\hbar^2 k^2}{2m} [C_1 \cos(kx) + C_2 \sin(kx)] = \frac{\hbar^2 k^2}{2m} \psi(x)$$

Comparing this with the r.h.s. of Eq. 5 immediately yields a connection between the energy eigenvalue E and the wave vector k :

$$(8) \quad E = \frac{\hbar^2 k^2}{2m}$$

The boundary condition 3 implies

$$(9) \quad \psi(0) = C_1 \cos(0) + C_2 \sin(0) = C_1 = 0$$

implying the solution is simply the sine function $\psi(x) \propto \sin(kx)$, where we still need to determine the value of the wave vector k . This is afforded by applying the boundary condition 4:

$$(10) \quad \psi(L) = 0 \Rightarrow C_2 \sin(kL) = 0$$

The equation $\sin x = 0$ is solved by any integer multiple of π : $x = \pi n$, $n = 0, \pm 1, \pm 2, \pm 3, \dots$. Therefore we have $kL = \pi n \Rightarrow k = \pi n/L$. However, the $n = 0$ option implies $k = 0$ and, hence, $\sin(kx) = \sin(0) = 0$, i.e., no particle at all. Thus $n = 0$ is not a valid option. Note further that the $(+n)$ and $(-n)$ options are equivalent. Indeed, a $(-n)$ solution is simply the negative of the corresponding $(+n)$ solution: $\sin(-\pi n/L) = -\sin(\pi n/L)$. If two solutions differ only by a multiplicative constant, they correspond to the very same microstate and, thus, are equivalent, as we discussed in the preceding Chapter. Thus, only the following values of the wave vector correspond to physically distinct microstates:

$$(11) \quad k_n = \frac{\pi n}{L}, \quad n = 1, 2, 3, \dots$$

where we used the index n to label the wave vectors corresponding to distinct states. The quantity n is an example of what we call a **quantum number**. Now that we know the allowed values of the wave vector, we can evaluate the corresponding energy eigenvalues, using Eq. 8:

$$(12) \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad n = 1, 2, 3, \dots$$

and the eigenfunction itself, as follows from Eqs. 9 and 10:

$$(13) \quad \psi_n(x) = A_n \sin(k_n x)$$

Where A_n is a fixed number, to be determined, and we are relieved to notice that the wave function can be made real-valued, since nothing prevents us from choosing the normalization constant to be real-valued. It is a general pattern that one always may—but does not have to!—choose the wave function of a bound state to be real-valued. To fix the value of A_n , we must specify the number of particles. Here we choose exactly one particle, for concreteness, and so for any $\psi(x)$:

$$(14) \quad \int_0^L p(x) dx = \int_0^L |\psi(x)|^2 dx = \int_0^L \psi^2(x) dx = 1$$

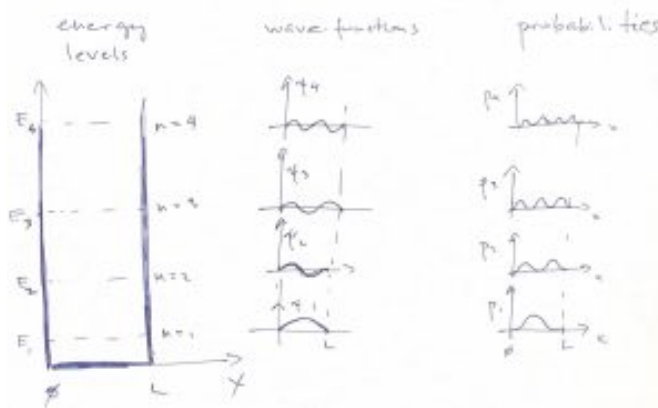
where we use the fact that our wavefunctions are real-valued and, so, $\psi^*(x) = \psi(x) \Rightarrow |\psi(x)|^2 = \psi^2(x)$. Thus for $\psi(x) = \psi_n(x)$, it must be true that

$$(15) \quad A_n^2 \int_0^L \sin^2\left(\frac{\pi n x}{L}\right) dx = 1$$

We can easily check, using the formula $\sin^2 x = (1 - \cos 2x)/2$ that the integral above is equal to $L/2$ irrespective of the value of n , and so $C_2 = (2/L)^{1/2}$. This yields

$$(16) \quad \psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi n x}{L}\right)$$

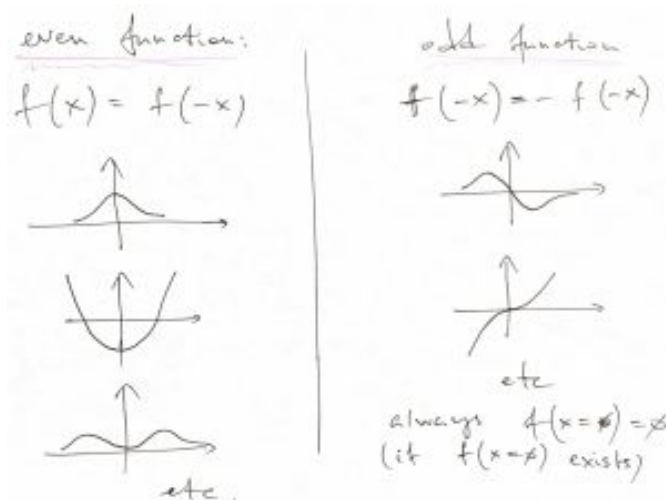
We graphically summarize these results below, where we show several low energy states and, on the side sketch the corresponding wave functions. The lowest energy state is called the ground state, the 2nd lowest energy state “the 1st excited state”, and so on:



We notice an important pattern that the wave function at the lowest energy is an even function w.r.t. reflection around the center of the well, while the next one is an odd function w.r.t. that reflection implying, then, that the wavefunction should have a node in the middle. The next energy state, again has an even eigenfunction, and so on. This important alternation pattern comes about because the potential energy $V(x)$ is *symmetric* with respect to reflection about a certain point in space. To understand this, it is convenient to place the origin into that special point. In the so chosen reference frame, the symmetry of the potential can be expressed mathematically as follows:

$$(17) \quad V(x) = V(-x)$$

In other words, the potential is an even function of its argument. Below, we exemplify both an even and odd function, for future reference:



Note that an odd function must always vanish at the origin, because an odd function is the negative of itself at the origin: $f(0) = -f(-0) = -f(0)$, which, then, implies $f(0) = 0$.

Now, take the time-independent Schrodinger Eqn:

$$(18) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E \psi(x)$$

and replace the argument x by its negative $-x$:

$$(19) \quad -\frac{\hbar^2}{2m} \frac{d^2}{(d(-x))^2} \psi(-x) + V(-x) \psi(-x) = E \psi(-x)$$

which amount to swapping the labels “positive” and “negative” for the directions in space. No actual changes to the system are inflicted. Since $(d(-x))^2 = (-dx)^2 = (dx)^2$ and $V(x) = V(-x)$, we obtain that the function $\psi(-x)$ obeys the same equation as the function $\psi(x)$:

$$(20) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(-x) + V(x) \psi(-x) = E \psi(-x)$$

On the other hand, since our relabeling of the direction in space did not create a distinct physical state, the “new” solution must be equal to the old one, up to a multiplicative constant:

$$(21) \quad \psi(-x) = C \psi(x)$$

and, likewise,

$$(22) \quad \psi(x) = C \psi(-x)$$

Substituting one of the two equations above into the other immediately yields:

$$(23) \quad C^2 = 1$$

or,

$$(24) \quad C = \pm 1$$

The $+1$ option implies the wave function is even: $\psi(x) = \psi(-x)$, while the -1 option implies the wave function is odd: $\psi(x) = -\psi(-x)$. To summarize, we have established that the wave function of a state bound inside a potential energy that’s an even function must be, itself, either even or odd. These ideas can be extended to other types of symmetry, such as those w.r.t. rotation around an axis, as in the molecule of benzene, or spatial translations, as in periodic crystals.

In addition to the aforementioned alternation in the parity of the wave-function, we also notice that for each next energy level, we get an additional node and an oscillation to the wavefunction, which is a general pattern.

According to Eqs. 11 and 12, both the momentum and energy of distinct microstates of a particle confined to a box are *quantized*. In other words, the momentum and energy of distinct microstates take values that are not continuously distributed but, instead, form a discrete set. The remarkable fact comes about, formally, because the wave function must vanish at the boundaries of the box. One can also think of the wave function as a standing wave (see the end of the last Chapter). In order for a wave to be standing, the size of the box must match an integer number of half-periods of the wave, c.f. Eq. 11.

Despite being a gross approximation, the particle in the box yields a really important pattern, namely, that the energy cost of confining, or, localizing the motion of a particle to an interval of finite length L in any spatial direction follows the following trend:

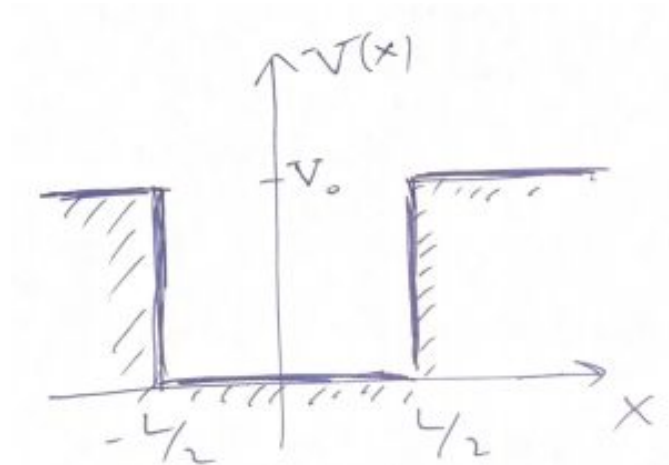
$$(25) \quad E_{\text{kin}} = \frac{p^2}{2m} \sim \frac{\hbar^2 n^2}{mL^2}$$

Various phenomena, such as the existence of metals and the circular shape of the benzene ring, ultimately come about because the electrons holding together those objects have minimized their kinetic energy by delocalizing over the whole system. More specifically, the only non-zero component of the energy of the particle in the box is the kinetic energy, as we have indicated with the label “kin”. Thus we conclude that by spatially “spreading” as much as possible, subject to the potential energy, the particle minimizes its kinetic energy.

The two main idealizations of the particle in box are that the potential (a) is too tall outside of the box and (b) is too steep. Let us address the first idealization by considering a box whose walls are of finite height V_0 , while the width is L as before:

$$(26) \quad V(x) = \begin{cases} 0, & -L/2 < x < L/2 \\ V_0, & x \leq -L/2 \text{ or } x \geq L/2 \end{cases}$$

It is somewhat more convenient to center the potential well at the origin:



Inside the well, where $V(x) = 0$, the Schroedinger equation reads

$$(27) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n = E_n \psi_n$$

while outside, where $V(x) = V_0$, we have

$$(28) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n + V_0 \psi_n = E_n \psi_n$$

The energy of the particle cannot have negative values since $V(x) \geq 0$ everywhere in space, while the kinetic energy must be positive at least somewhere. Thus we observe that just like in the above case of the infinitely deep well, the solutions inside the well are oscillating functions of the coordinate. Still, there is the difference that the wave function no longer vanishes at the edges of the well, since $V(x)$ is finite there. The eigenfunctions must be either even or odd functions, as already discussed, while we know that the cosine is an even function while the sine is an odd function w.r.t. reflection about the origin. Thus we infer, by symmetry, that the ground state must be a cosine function:

$$(29) \quad \psi_1(x) = C_1 \cos(k_1 x)$$

the first excited state is a sine function:

$$(30) \quad \psi_2(x) = C_2 \sin(k_2 x)$$

and so forth. Inserting these Eq. 27 implies that, as in the case of the infinitely deep well, we have

$$(31) \quad E_n = \frac{\hbar^2 k_n^2}{2m}, \quad n = 1, 2, 3, \dots$$

however the quantization conditions for the wave vector k_n are similar but no longer as simple as in Eq. 11, nor are the conditions for the normalization constants C_n because the wave function does not vanish outside the well. In any event, the earlier made notions regarding the symmetry of the wavefunctions and the number of nodes inside the well still hold.

How does the wave function behave outside the well? Here we have two options. For $E_n < V_0$, Eq. 32 gives an eigenvalue problem where the eigenvalue is now *negative*:

$$(32) \quad -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n = (E_n - V_0) \psi_n$$

This equation is solved not by a combination of sine and cosine functions but, instead, by the usual exponential function: $e^{+\kappa_n x}$ or $e^{-\kappa_n x}$. Inserting these into Eq. 32 yields:

$$(33) \quad \frac{\hbar^2 \kappa_n^2}{2m} = (V_0 - E_n)$$

and, hence,

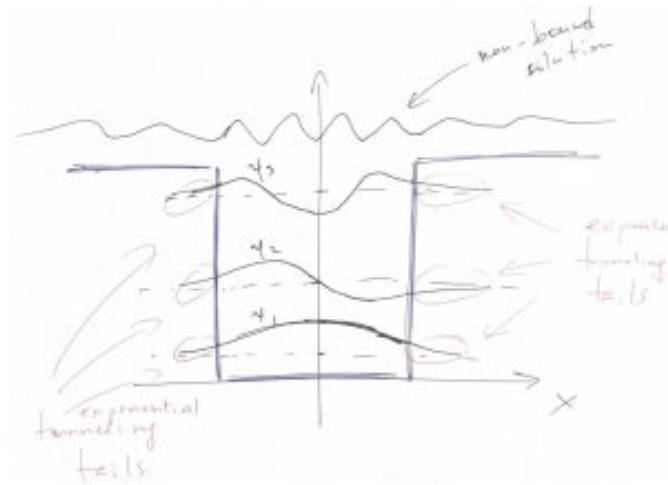
$$(34) \quad \kappa_n = \sqrt{2m(V_0 - E_n)}/\hbar$$

where chose κ_n to be the positive root for concreteness. To make sure the wave function is normalizable, i.e., we are dealing with a finite number of particle, we must correctly choose which of the two exponentials is used to the right of the well and which one to the left:

$$(35) \quad \psi_n(x) = B_n e^{-\kappa_n x}, \quad x > L/2$$

$$(36) \quad \psi_n(x) = D_n e^{+\kappa_n x}, \quad x < -L/2$$

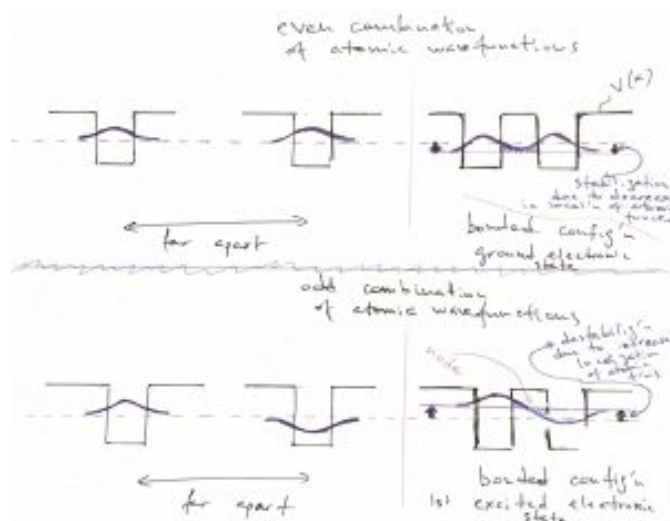
Thus we obtain that the wave function does not vanish in the region of space where the values of the energy are less than the potential energy! Note that a classical particle would not be able to penetrate regions where the total energy is less than the potential energy because it would cause the kinetic energy to be negative. But the kinetic energy of a classical particle, $mv^2/2$ is an intrinsically non-negative quantity. Though the wavefunction is seen to penetrate that classically-forbidden region, it still decays there rather rapidly, exponentially in fact. We graphically summarize these notions below:



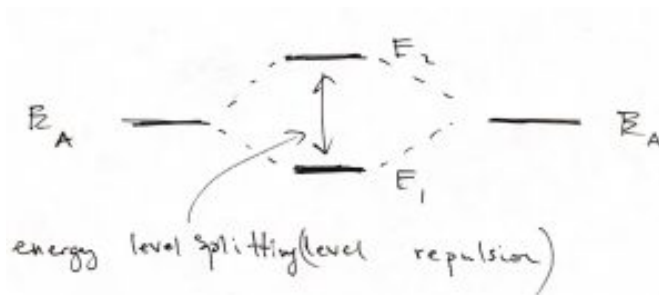
Finally, when the particle's energy is greater than the highest value of the potential energy: $E_n > V_0$, the wavefunction becomes wave-like throughout the whole space and, in fact, is best described as a wave packet. The energies values of a wave packet are not quantized but, instead, form a continuum.

The tails of the wavefunction that penetrate the classically forbidden region represent an intrinsically wave-like phenomenon. These tails are often called *tunneling tails* to signify that the particle can penetrate, or “tunnel” under a potential wall.

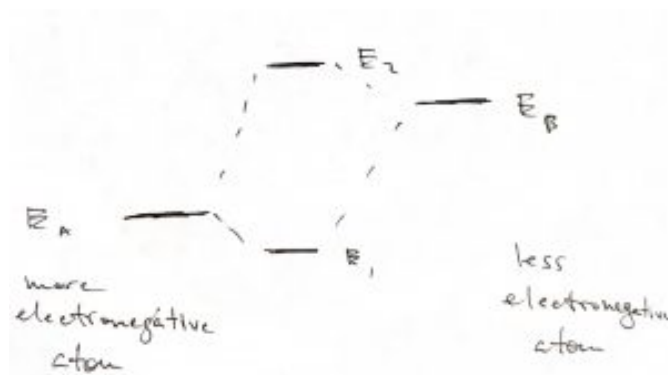
The above example of a potential well with finite walls sets us up for discussing the most basic features of molecular binding. Let us now consider *two* identical potential wells, each corresponding to the bounding potential of an atom. (Generally, the bounding potential corresponds to a positive nucleus dressed by some electrons that are bound so strongly that they are not affected much by the proximity of other atoms.) In the Figure below, we consider four configurations. The l.h.s. corresponds with the two atoms being far apart, while the r.h.s. with those two atoms being close. Note that we can consider, a priori, a situation where the two atomic wavefunctions (or “orbitals”) have the same sign or have opposite signs. The top of the figure corresponds with the former, “even” possibility, while the bottom of the Figure corresponds with the latter, “odd” possibility:



We observe that for the even combination (the top of the Figure), bringing in the other atom allows each of the individual orbitals to extend a little further toward the other atom, because there is now a low energy region available in that direction. As a result, each of the atomic orbitals can lower its kinetic energy, by virtue of Eq. 25. This is in addition to the already mentioned lowering of the potential energy. Hence the overall energy is lowered, too. This stabilization is, ultimately, the origin of the stability of the molecule, relative to the non-bound state, where the atoms are far apart. In more physical terms, this stabilization in the presence of another atom comes about electrons on one atom “feel” the attraction from the other atom and can lower their energy by visiting that part of space, see also below. The odd combination of the atomic function does the opposite thing: Because this combination must have a node and, thus, vanishes in the middle, the individual wavefunctions now extend out *less* than they would in the absence of the other atom. As a result, both the kinetic energy goes up (the localization length is now somewhat smaller) and the potential energy is not as low because the tunneling tails do not extend toward the low energy regions centered on the other atom. Thus the total energy of this microstate is higher than that of an individual atom, let alone the energy of the binding orbital. This microstate is the first excited state. Below we graphically summarize the above notions of the stabilization/destabilization of the molecular orbitals, relative to the atomic orbitals:

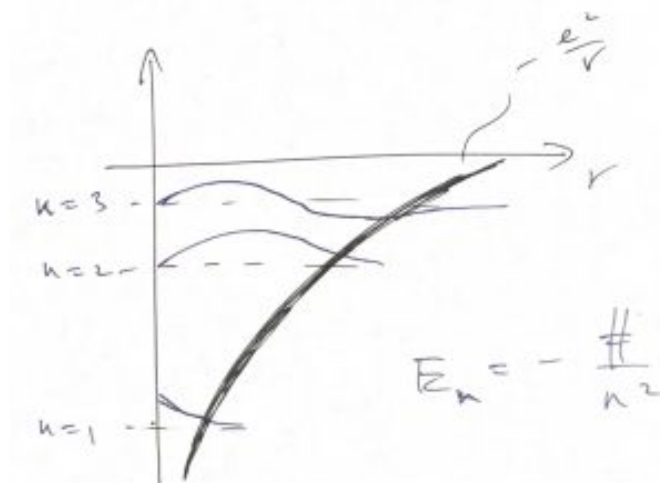


When the two atoms are not identical, the situation is similar in that the ground state orbital is more stable than that on the more electronegative atom while the excited state orbital is less stable than the orbital on the less electronegative atom:

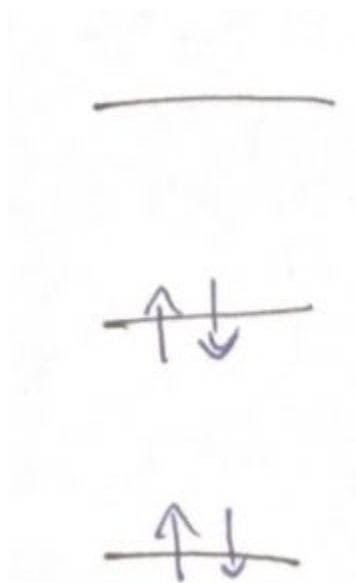


The gap, or “splitting”, between the ground state and 1st excited state of the molecule is a very general phenomenon. We see it comes about because of the possibility of tunneling between bound states, which would not be possible in Classical Mechanics. Because of this splitting, we believe that the ground state of any physical system must be non-degenerate. Indeed, if there were two or more lowest energy states, then the mutual tunneling between these lowest energy states would mix them up and cause one orbital to split off toward lower yet energies. This fact of the uniqueness of the ground state then yields the 3rd Law of Thermodynamics.

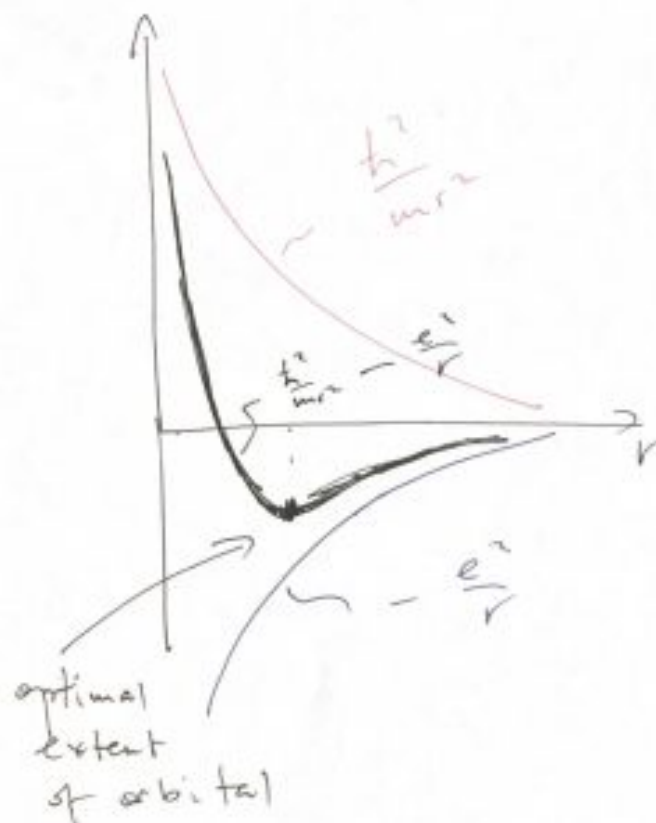
We have now most of the ingredients to qualitatively discuss of how the finite size of an atom comes about and the nature of chemical bonding. Below we sketch some of the energy levels and wave functions for the motion of the negatively charged electron in the attractive field of a positively charged nucleus:



As before, the wave function is a standing wave in the classically allowed region, where the potential energy does not exceed the total energy but decays exponentially in the classically forbidden region. In the simplest way of discussing this, the energy levels form a “ladder” whose steps can accommodate electrons. The electrons possess an internal degree of freedom, called the spin, in addition to the degree of freedom corresponding to the motion in the 3D space. The quantum number for the spin has only two distinct values, corresponding to spin up and down. According to Pauli’s exclusion principle, whose discussion is beyond the scope of this course (but see the bonus discussion at the end), no two electrons can possess the same set of quantum numbers. Thus we can put at most two electrons into one orbital, but only if their spins have distinct values. Thus we can “build” up an atom by placing electrons on the steps of the ladder starting from the lowest energy one:



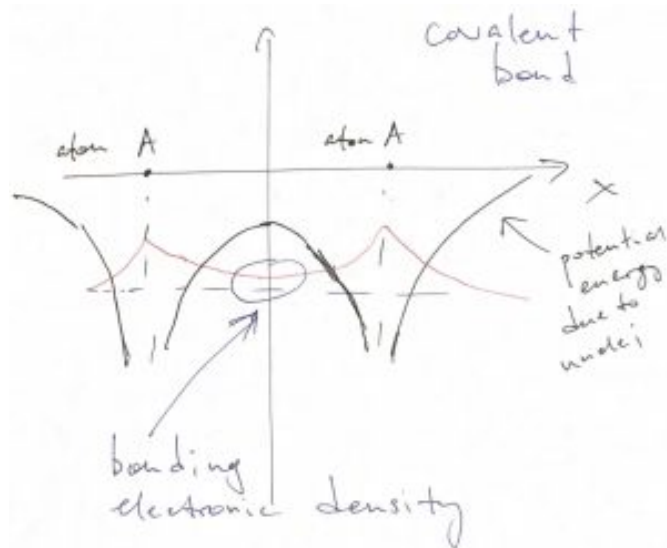
The finite size of an atom comes about for the following reason. On the one hand, the energy of the Coulomb attraction, $V(r) = -e^2/r$ favors the ever closer separations between the electron and the nuclei, since the potential energy is minimized (and, in fact, becomes infinitely negative) as $r \rightarrow 0$. On the other hand, localizing the electron to a region of size r is subject to the penalty of raising the kinetic energy, \hbar^2/mr^2 , up to a numerical factor, per Eq. 25. Thus the actual extent of the electronic orbital is controlled by two competing factors and is found by optimizing the total energy $\hbar^2/mr^2 - e^2/r$, which we graphically illustrate below:



To be clear, this is a qualitative argument. One can obtain very accurate solutions for the electronic wave functions in many cases, but the complexity of the solution can obscure the relatively simple meaning of the effect. To summarize, atoms are finite because (a) the orbitals are finite in extent and (b) because one can put at most

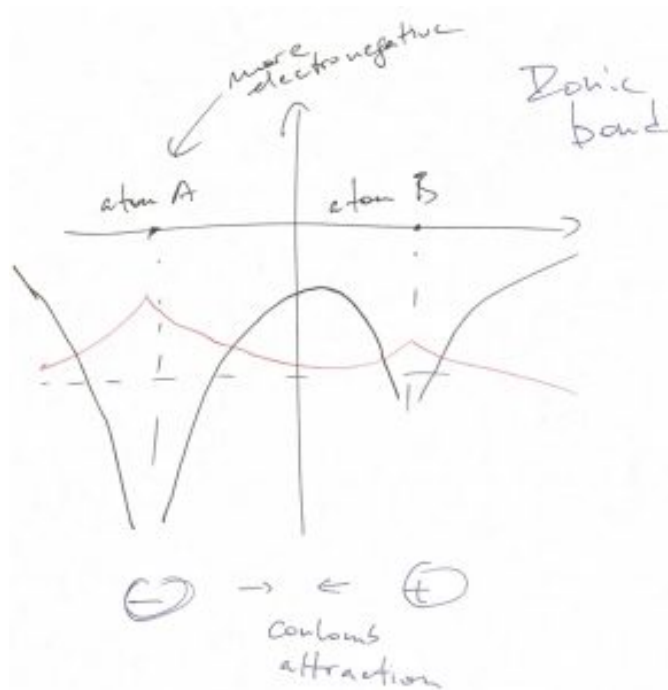
two electrons in one orbital. As a result, when two atoms come close together, the electrons from one atom cannot jump onto any of the orbitals centered on the other atom, if the latter orbitals are already filled.

They *can* however jump so if those orbitals are not filled. According to the qualitative picture of the atomic levels mentioned above, those so called “valence” orbitals correspond to less deep energy levels and, at the same time, are more extended than the deep orbitals. It is instructive to sketch the potential felt by a valence electron in the presence of not one, but two nuclei. First, we assume the two nuclei are identical:



We observe that the ground state orbital is small in the inter-nuclear space because the electron reaches there by tunneling. Despite being small, the wave function is non-vanishing. The corresponding, rather modest amount of negative charge in the inter-nuclear space actually suffices to bind such atoms together. This type of bond is called *covalent*. It has a characteristic feature of being rather directional, as the bonding electronic density is usually distributed around atoms anisotropically, i.e. not in a spherically-symmetric fashion.

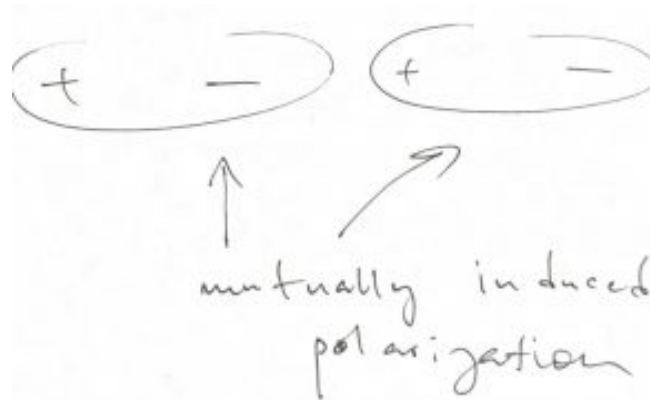
When the two atoms are not identical, then much of the ground state wave function will be centered on the more electronegative atom:



In this case, the valence electrons will flock to the more electronegative atom. As a result, the bond can be well

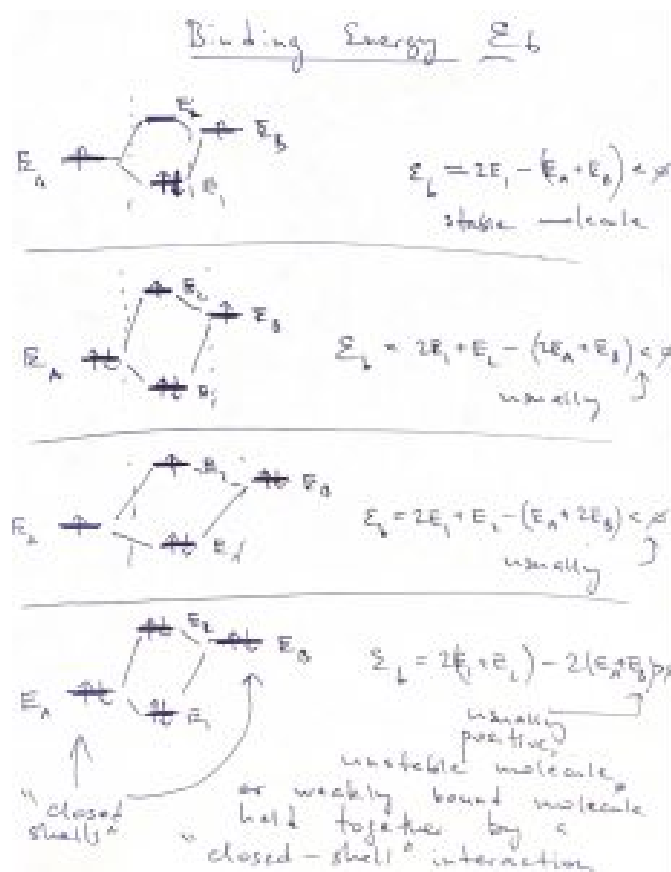
thought of as resulting from Coulomb attraction between a positively and negatively charged objects, both objects exhibiting rather isotropic charge distribution. The resulting type of bond is often referred to as an *ionic* bond.

The preceding situations are realized when the constituent atoms each contribute an orbital and one electron to the bond. What happens when each atom contributes one orbital that is filled by two electrons? In such cases, neither the covalent bond, nor the ionic bond can realize. Instead, the bond will be of much, weaker nature and results from a mutually induced polarization:



We call such bonds secondary, or closed-shell interactions, the word “closed-shell” referring to the fact that the orbitals in question are filled. The important hydrogen is, formally, an example of a closed-shell interaction and happens to be rather directional because the orbitals involved are rather anisotropic.

The notion of “building up” the atomic orbitals applies to the molecular orbitals as well. We evaluate the energy of an electronic configuration by counting the electrons residing in an orbital and multiplying that by the energy of the orbital:



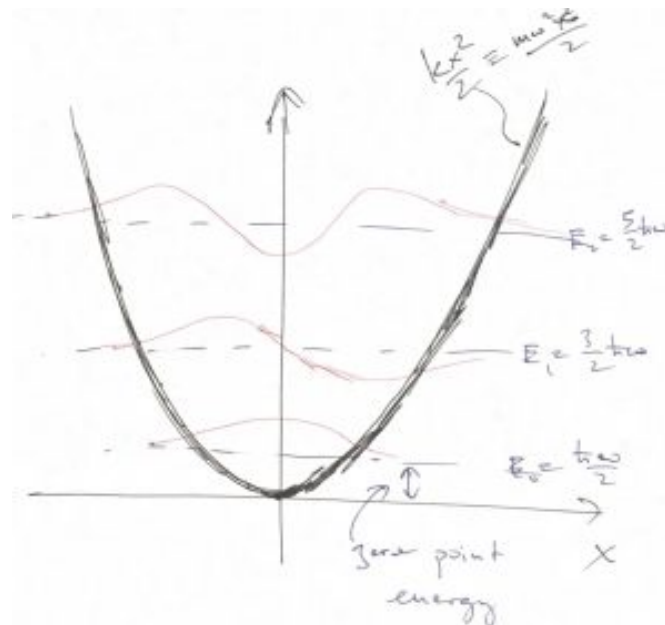
Again, we remind that at most two electrons can “sit” in one orbital. If the orbital is completely filled, i.e.,

contains two electrons, the electrons must have oppositely oriented spins. Note we have completely ignored the fact that the energies of the orbitals will generally depend on both the total number of electrons in the system and how they are distributed among the orbitals. These are rather complicated matters that we cannot do justice to in this Course; they are however important and form the subject of Quantum Chemistry.

Finally we touch upon the potential energy of a harmonic oscillator:

$$(37) \quad V(x) = \frac{kx^2}{2} \equiv \frac{m\omega x^2}{2}$$

where k is the spring constant and $\omega \equiv (k/m)^{1/2}$ the oscillator's frequency. This model is important in Physical Chemistry because it can be used to describe vibrations of chemical bonds. Below we sketch several lowest energy levels alongside the corresponding orbitals:



Because the quadratic potential function extends all the way to infinity, all of the states are bound and so the energies of the microstates form a discrete set:

$$(38) \quad E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

As was the case for all the models discussed above, the ground state energy is above the bottom of the potential: $E_0 = \frac{\hbar\omega}{2}$. This “excess” energy is called the zero-point energy and has observable consequences. For instance, it contributes to the formation enthalpy of solids and molecules alike.

Finally, we invoke the notion from Eq. 11 one more time to note that the typical value of momentum of a particle is connected to the size of the region to which the particle is confined

$$(39) \quad |p| \sim \frac{\hbar n}{L}$$

Since the average momentum is zero—the particle is not going anywhere—this equation can be re-written for the deviation δp of the momentum from its average value:

$$(40) \quad \delta p \sim \frac{\hbar n}{L}$$

At the same time, the box size L can be thought of as the uncertainty δx in the position of the particle. Thus we get $\delta p \delta x \gtrsim \hbar$, since $n \geq 1$. A more accurate estimate is

$$(41) \quad \delta p \delta x \geq \hbar/2$$

and is known as Heisenberg's uncertainty principle. It is yet another way of discussing the wave-like nature of what may seem like a particle when experimental resolution is lacking.

Bonus discussion: We also notice the remarkable property of the eigenfunctions of our Hamiltonian that:

$$(42) \quad \int_0^L \psi_m(x) \psi_n(x) dx = \begin{cases} 1, & \text{if } m = n \\ 0, & \text{if } m \neq n \end{cases}$$

This is a general pattern that makes it easy to see that one may combine more than one eigenstate of the Hamiltonian to put together an infinite variety of wavefunctions for our system:

$$(43) \quad \psi(x) = \sum_n B_n \psi_n(x)$$

where the summation is over the quantum number n , which is $n = 1, 2, 3, \dots$ in this specific case, and the constants B_n must be chosen to preserve the normalization. This notion, then, fleshes out the statement we made in the preceding Chapter that one may present an initial state of a quantum-mechanical system in terms of the harmonics, each of which, then, oscillates with its own frequency.

The aforementioned Pauli exclusion principle is yet another realization of the importance of symmetry effects in Quantum Mechanics. We have already considered a special case where the potential energy for 1D motion is an even function of its argument. In this case we saw that a half of the orbitals must have a node at the origin. Now consider a very different type of symmetry. Imagine two identical particles, whose coordinates are \vec{r}_1 and \vec{r}_2 , respectively. Each particle is subject to an external potential $V(\vec{r})$. In addition, the two particles may interact via some interaction potential $V_{\text{int}}(|\vec{r}_1 - \vec{r}_2|)$ that depends only on the mutual distance $|\vec{r}_1 - \vec{r}_2|$. We add these potential energies to the kinetic energies of the two particles to put together the Hamiltonian for this system:

$$(44) \quad \hat{H}(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(\vec{r}_1) + V(\vec{r}_2) + V_{\text{int}}(|\vec{r}_1 - \vec{r}_2|)$$

where $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the 3D analog of the second derivative w.r.t. the spatial coordinate. The above Hamiltonian has a special property of being symmetrical w.r.t. the interchange of the particles' labels: $1 \leftrightarrow 2$:

$$(45) \quad \hat{H}(\vec{r}_1, \vec{r}_2) = \hat{H}(\vec{r}_2, \vec{r}_1)$$

One can now perform steps analogous to those that led to Eqs. 21 and 22 and show that the Schroedinger equation satisfied by the function $\psi(\vec{r}_1, \vec{r}_2)$:

$$(46) \quad \hat{H}(\vec{r}_1, \vec{r}_2) \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2)$$

is equally well satisfied by the function $\psi(\vec{r}_2, \vec{r}_1)$:

$$(47) \quad \hat{H}(\vec{r}_1, \vec{r}_2) \psi(\vec{r}_2, \vec{r}_1) = E \psi(\vec{r}_2, \vec{r}_1)$$

Since relabeling the particles does not correspond to physical changes, we conclude such relabeling will at most lead to the wavefunction being multiplied by a constant factor:

$$(48) \quad \psi(\vec{r}_1, \vec{r}_2) = C \psi(\vec{r}_2, \vec{r}_1)$$

and, likewise,

$$(49) \quad \psi(\vec{r}_2, \vec{r}_1) = C \psi(\vec{r}_1, \vec{r}_2)$$

This leads to $C^2 = 1$, and, consequently, to either

$$(50) \quad C = +1$$

or

$$(51) \quad C = -1$$

The latter possibility is particularly interesting in that it implies that the wave function changes its sign upon interchanging the particles' identities:

$$(52) \quad \psi(\vec{r}_2, \vec{r}_1) = -\psi(\vec{r}_1, \vec{r}_2)$$

Substituting $\vec{r}_2 = \vec{r}_1 = \vec{r}$ immediately yields that the wave function must have a node, i.e., the chances of finding the particles both at the same place *vanish*:

$$(53) \quad \psi(\vec{r}, \vec{r}) = -\psi(\vec{r}, \vec{r}) \Rightarrow \psi(\vec{r}, \vec{r}) = 0$$

Informally speaking, particles whose exchange properties fall under the rule [51](#) cannot be in one spot at the same time! It might not be a priori obvious why it should be so, but there are apparently particles that obey the rule [50](#) and particles that obey the rule [51](#). The former case is known as the Bose-Einstein statistics, while the latter case as Fermi-Dirac statistics. The electrons happen to obey the Fermi-Dirac statistics, hence the Pauli exclusion principle. This, as we saw earlier in the Chapter is absolutely necessary for atoms to exist as rigid entities. Indeed, electrons can also have two distinct values of the spin and so one cannot put more than two electrons into an orbital, one electron per distinct value of the spin. Consequently, two filled orbitals will repel from each other thus making atoms rather behave like rather rigid objects. While it is possible to squeeze the orbitals themselves, using high pressures, this comes at a cost of increasing the kinetic energy of the electrons, per Eq. [25](#).