A Thermal Physics Primer

(based on Daniel V. Schroeder's *Thermal Physics*)

Sharon J. Gerbode

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Abstract

This document is intended to be used as an introduction to the elements of thermal physics that are most relevant to the research conducted in the Gerbode Lab. This primer is meant to be approachable and even welcoming to a 'typical' rising sophomore at Harvey Mudd College. It is *not* intended to be used as a quick-reference source of facts, but rather as a vehicle for providing intuition for some of the fundamental concepts in thermal physics. I am grateful to Paul Jerger (HMC '15) for his efforts to understand and edit this first draft.

Contents

1 The canonical cartoon of thermal physics

Let's start this whole document with the cartoon that will come up again and again in thermal physics. Consider two systems containing many particles with a distribution of energies. If the systems are in thermal contact, they'll eventually reach equilibrium.

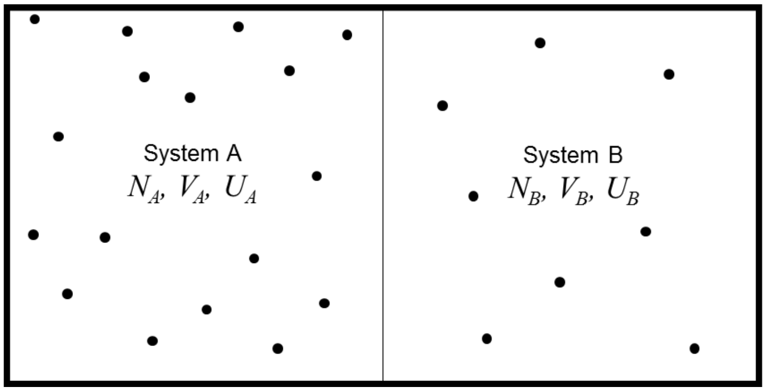

Figure 1: Schematic of two systems in thermal contact. The thick line indicates isolation from the rest of the world, and the thin line allows for interactions between the systems.

N: Number of particles
V: Volume of system
U: Total energy of system is the sum of the particles' energies ($\sum_{i=1}^{N} U_i$)

There are different types of equilibrium:

Type of equil.	Exchanged quantity	What is equal?
Thermal	Energy	T
Mechanical	Volume	P
Diffusive	Particles	μ

More about T, P, and μ soon. First we need to learn about entropy. For that, let's start by counting states and defining multiplicity.

2 Multiplicity and such

Imagine flipping three coins: a penny, a nickel, and a dime. What are all the possible outcomes?

	Penny	Nickel	Dime
3 heads (0 tails)	H	H	H
	H	H	T
2 heads (1 tails)	H	T	H
	T	H	H
	H	T	T
1 heads (2 tails)	T	H	T
	T	T	H
0 heads (3 tails)	T	T	T

There are 8 distinct outcomes; we will call each of these a "microstate". However, there are only four global states (for example, 2 heads); we call each of these a "macrostate". The number of microstates in each macrostate is called its multiplicity, denoted by Ω. In our coin example,

$$\begin{aligned}\Omega(3\text{ heads}) &= 1\\ \Omega(2\text{ heads}) &= 3\\ \Omega(1\text{ heads}) &= 3\\ \Omega(0\text{ heads}) &= 1\end{aligned}$$

and $\Omega(all) = 1 + 3 + 3 + 1 = 8$ is the total number of microstates. Thus the probability of n heads is $\Omega(n)/\Omega(all)$. For a system of N coins, the multiplicity of a macrostate with n heads is:

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} \equiv \binom{N}{n}$$

Coins that randomly take on one of two possible states – heads or tails – are an example of a "two-state system". There are many other examples of two-state systems in physics; everyone's favorite is spins that may either point up or down, for quantum mechanical reasons.

3 Einstein solids

An Einstein solid is a slightly more complicated model that applies to many physical systems, despite its simplicity.

Imagine a collection of N "oscillators", that is, N particles moving in locally quadratic potential energy wells. Each oscillator has some positive integer number of energy units, each with energy U_0. The *total* number of energy units of the entire collection of N oscillators is q, so the total energy of the entire collection of oscillators is qU_0.

Example: Einstein solid with $N = 3$ oscillators, for $q = 0, 1, 2$:

	Osc. #1	Osc. #2	Osc. #3	
$q = 0$	0	0	0	$\Omega(N = 3, q = 0) = 1$
$q = 1$	1	0	0	$\Omega(N = 3, q = 1) = 3$
	0	1	0	
	0	0	1	
$q = 2$	2	0	0	$\Omega(N = 3, q = 2) = 6$
	0	2	0	
	0	0	2	
	1	1	0	
	1	0	1	
	0	1	1	

The general formula for the multiplicity of an Einstein solid with N oscillators and q total energy units is:

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!} \equiv \binom{q + N - 1}{q}$$

This works great for small N, but in stat mech, we'll deal with very large numbers, such as the number of particles in a thermodynamic crystal($\sim 10^{23}$). Also, q is typically much much larger than N (i.e. each oscillator has many more than one available energy unit). In the limit of large N and $q \gg N$,[1] we may make use of the very handy Stirling's approximation:

$$N! \approx N^N e^{-N}\sqrt{2\pi N},\ N \gg 1 \qquad \text{or} \qquad \ln(N!) \approx N\ln(N) - N$$

The square root factor in the first version of the approximation is usually dropped, since it is negligible compared to N^N. Using this approximation, $\Omega(N, q)$ can be written as:

$$\Omega(N, q) \approx e^N \left(\frac{q}{N}\right)^N = \left(\frac{eq}{N}\right)^N$$

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[1] In this limit of large q and N, the discrete mutiplicity $\Omega(N, q)$ becomes a continuous function of N and q.

4 Interactions between 2 Einstein solids: Defining temperature

Suppose that we have two systems:
System A, with N_A oscillators and q_A energy units
System B, with N_B oscillators and q_B energy units

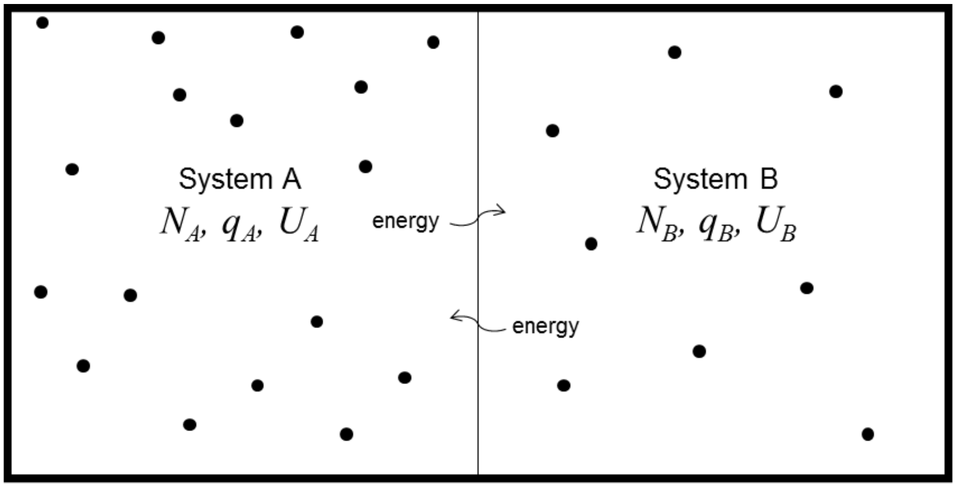

Figure 2: Schematic of two 'weakly coupled' systems A and B that can exchange only energy.

Imagine A and B are 'weakly coupled,' meaning they can exchange energy with each other, but are isolated from the rest of the world. This situation is pictorially represented in Fig. 2. How do we define the macrostate of the combined system? The instantaneous macrostate is defined by the instantaneous values of q_A and q_B. These will vary so that the total energy of the system is conserved, ie. $q_A U_0 + q_B U_0 = q_{total} U_0 = \text{constant}$. What are the multiplicities Ω_A and Ω_B of each individual system?

$$\Omega_A = \frac{(q_A + N_A - 1)!}{q_A!(N_A - 1)!}$$

$$\Omega_B = \frac{(q_B + N_B - 1)!}{q_B!(N_B - 1)!}$$

For each of the Ω_A microstates available to A, there are Ω_B microstates available to B, since the systems have independent ensembles of oscillators. Thus the total multiplicity of the combined system is $\Omega(q_A, q_B) = \Omega_A \Omega_B$.

Let's consider a tractable example. The macrostates and multiplicities of the combined system with $N_A = N_B = 3$ and $q_A + q_B = 6$ are:

q_A	Ω_A	q_B	Ω_B	$\Omega(q_A, q_B)$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
				462

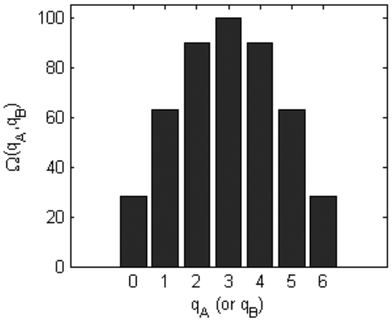

Figure 3: Multiplicity *vs.* q_A, for $N_A = N_B = 3$ and $q_A + q_B = 6$.

There are a total of 462 microstates available to the combined system. At this point, we make a big assumption, that over very long time scales, energy is passed around randomly between microstates in such a way that each microstate is equally likely. This is called the "**Fundamental assumption of statistical mechanics**:"

In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

For our little tractable system, this assumption would imply that if we wait long enough until the combined system reaches equilibrium, the macrostate with $q_A = q_B = 3$ is the most likely macrostate, with probability

$$P(q_A = 3, q_B = 3) = \frac{\Omega(3,3)}{\Sigma\Omega} = \frac{100}{462} \approx 22\%$$

Let's consider a larger (but not quite 10^{23} big!) system of two weakly coupled Einstein solids with

$$N_A = 300 \quad N_B = 200 \quad , \quad q_A + q_B = 100$$

Calculating multiplicities for this system is a bit more laborious, but with the help of a computer it can easily be done. The results are shown in the table below.

q_A	Ω_A	q_B	Ω_B	Ω_{total}
0	1	100	2.8×10^{81}	2.8×10^{81}
1	300	99	9.3×10^{80}	2.8×10^{83}
2	45150	98	3.1×10^{80}	1.4×10^{85}
3	4545100	97	1.0×10^{80}	4.6×10^{86}
4	3.4×10^{8}	96	3.3×10^{79}	1.1×10^{88}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
59	2.2×10^{68}	41	3.1×10^{46}	6.8×10^{114}
60	1.3×10^{69}	40	5.3×10^{45}	6.9×10^{114}
61	7.7×10^{69}	39	8.8×10^{44}	6.8×10^{114}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
100	1.7×10^{96}	0	1	1.7×10^{96}
				9.3×10^{115}

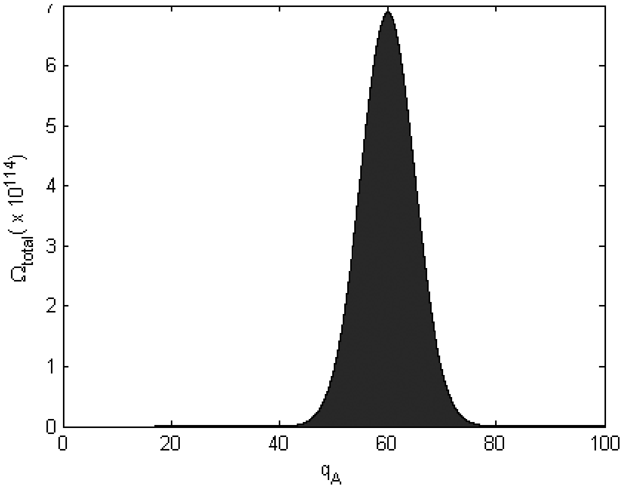

Figure 4: Combined macrostate multiplicity $\Omega(q_A, q_B)$ *vs.* q_A for a system with $N_A = 300$, $N_B = 200$, $q_A + q_B = 100$.

Wow – those multiplicities got big fast! Let's think about some probabilities. The most likely macrostate has $q_A = 60$, $q_B = 40$. The probability that the combined system is in this macrostate is only about 7%, but this probability falls sharply on either side of $q_A = 60$. For example, $P(q_A < 10) < 10^{-20}$!

Now let's imagine that the combined system started in a very unlikely state with $q_A = 0$ and $q_B = 100$. After some time has passed (i.e. after energy has been randomly passed around), energy will have moved from solid B to solid A, simply because there are more states with energy distributed more evenly between A and B. This spontaneous flow of energy is called "heat," and in very large systems (i.e. q and $N \gg 1$) it continues as the system approaches its *most likely macrostate.* Thus, the system evolves in such a way as to increase multiplicity – this is called the "2^{nd} Law of Thermodynamics."

Clearly this "law" is just a statement about probabilities - there is no reason that energy ("heat") is forbidden from flowing to a state with lower multiplicity; it is just very unlikely!

The statement that in equilibrium the combined system will be in the macrostate with the highest multiplicity becomes precisely true in the "thermodynamic limit," where $q,\ N \to \infty$. Let's revisit our two Einstein solids in this limit, where we can reliably estimate $\Omega(N,q) = (\frac{eq}{N})^N$.

In this limit, the multiplicity of a given macrostate is

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

where each solid has N oscillators. Plot this and see that it is sharply peaked with max value $\Omega_{max} = (\frac{e}{N})^{2N}(\frac{q}{2})^{2N}$ at $q_A = q_B = \frac{q}{2}$.

In the thermodynamic limit, the probability of being in any state besides the most likely macrostate becomes vanishingly small! Formally, in the thermodynamic limit, a system in thermodynamic equilibrium is in the most likely macrostate, namely, the macrostate that maximizes multiplicity Ω. We can write this statement as the condition for thermodynamic equilibrium:

In equilibrium between two systems A and B with total energy $q_{total}U_0$, system A will have energy q^*U_0 (and B will thus have $q_B U_0 = (q_{total} - q^*)U_0$), where q^* is the value that maximizes the multiplicity of the macrostate of the combined system, $\Omega(q_A, q_B)$. Mathematically, this condition is written as:

$$\text{In equilibrium,} \quad \left.\frac{\partial \Omega(q_A, q_B)}{\partial q_A}\right|_{q^*} = 0 \quad \left(\text{and } \frac{\partial^2 \Omega(q_A, q_B)}{\partial q_A^2} < 0\right)$$

Since $\Omega(q_A, q_B) = \Omega_A(q_A)\Omega_B(q_B)$, the condition becomes:

$$\left.\frac{\partial}{\partial q_A}\left(\Omega_A(q_A)\Omega_B(q_B)\right)\right|_{q^*} = 0$$

By the product rule, this becomes:

$$\left[\frac{\partial \Omega_A(q_A)}{\partial q_A}\Omega_B(q_B) + \frac{\partial \Omega_B(q_B)}{\partial q_A}\Omega_A(q_A)\right]_{q_A = q^*} = 0$$

and since $q_B = q_{total} - q_A$:

$$\left[\frac{\partial \Omega_A}{\partial q_A}\Omega_B - \frac{\partial \Omega_B}{\partial q_B}\Omega_A\right]_{q_A = q^*} = 0$$

Thus we see that in equilibrium

$$\frac{\partial \Omega_A}{\partial q_A}\Omega_B = \frac{\partial \Omega_B}{\partial q_B}\Omega_A$$

or equivalently

$$\frac{1}{\Omega_A}\frac{\partial \Omega_A}{\partial q_A} = \frac{1}{\Omega_B}\frac{\partial \Omega_B}{\partial q_B}$$

Noting that $\frac{\partial}{\partial x}(\ln f(x)) = \frac{1}{f(x)}\frac{\partial f}{\partial x}$ by the chain rule, we see that in equilibrium

$$\frac{\partial}{\partial q_A}\ln \Omega_A = \frac{\partial}{\partial q_B}\ln \Omega_B \quad , \quad \begin{array}{c} q_A = q^* \\ q_B = q_{total} - q_A \end{array}$$

This is simply a statement that multiplicity is maximized in thermal equilibrium. Throwing in a factor of k_B/U_0 on both sides yeilds

$$\frac{\partial}{\partial U_A}(k_B \ln \Omega_A) = \frac{\partial}{\partial U_B}(k_B \ln \Omega_B)$$

where k_B is Boltzmann's constant.

If we now define the quantity $S_A = k_B \ln \Omega_A$ as the entropy of system A, and similarly $S_B = k_B \ln \Omega_B$, then we see that in equilibrium

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad , \quad U_A = U^* \text{ and } U_B = U_{total} - U^*$$

Finally, defining temperature by $\frac{1}{T} = \frac{\partial S}{\partial U}$, we see that indeed, the two temperatures are equal when the systems are in thermal equilibrium:

$$\frac{1}{T_A} = \frac{1}{T_B}$$

Okay, so let's go back to that chart from the first page:

Type of equil.	Exchanged quantity	What is equal?
Thermal	Energy	T
Mechanical	Volume	P
Diffusive	Particles	μ

We have now seen, with the example of two interacting Einstein solids, how when energy is randomly exchanged between equally likely microstates, when thermal equilibrium is reached, the combined system will be in the macrostate with the highest multiplicity. Consequently the two constituent Einstein solids will be at the same temperature T. Along the way we made some important thermodynamic definitions that are worth reiterating. The entropy S and temperature T are defined as:

$$S = k_B \ln \Omega \tag{1}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{2}$$

Here we have introduced the important partial derivative notation $\left(\frac{\partial f}{\partial x}\right)_{y,z}$, which means the derivative of the function f with respect to x holding only the quantities y and z constant. Similarly, if one imagines two interacting systems whose energies are fixed but can exchange volume so that the total volume is held fixed, one will find using analogous arguments that the equilibrium pressure P that is constant between the two systems is defined by:

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{3}$$

For two interacting systems that share a total number of oscillators or energy-carrying 'particles', a similar line of reasoning defines the chemical potential μ:

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{4}$$

The above are called *thermodynamic relations.* We will return to the topic of pressure and chemical potential in later sections.

5 The Ideal Gas *(optional)*

Note: If you are okay with just believing the Ideal Gas Law and want to get on with your life, you can just read the first paragraph and then skip ahead to the next section.

Like many physical "ideals" the ideal gas only truly exists in one's imagination. The idea is that there are noninteracting pointlike particles each of mass m contained in some box of volume V that bounce elastically off of the walls of the box (and also off of each other). The particles have random positions and velocities, and possess only kinetic energy; there is no potential energy – no gravity, no electromagnetic field, etc. Since all particle collisions are elastic, the total energy of the ideal gas is conserved, although it does get exchanged between the particles via their collisions. Momentum is delivered to the box via collisions and is thus not conserved for the ideal gas particles (strictly speaking, the magnitude of the total momentum is conserved, but its direction can change). You may have noticed that right away we are presented with an inconsistency: how can the 'noninteracting' particles bounce off one another? Well, in our microscopic model of an ideal gas, we only like to think about the particles colliding long enough for the system to come to equilibrium, ie. for the kinetic energy to be randomly passed around between particles in the ideal gas. Then forever after, we'll ignore any interactions to make it easier to count microstates.

Actually, how do we count microstates in this system? Hmm... this is trickier than counting microstates in Einstein solids, because we no longer have discrete energy levels. What do we have instead? To be specific, let's consider a cube-shaped box with side length L containing N ideal gas particles with a total energy $U = \sum_{i=1}^{N} \frac{1}{2} m v_i^2$. What are all the possible microstates of this ideal gas? A couple of instantaneous microstates are pictured in Fig. 5. In Fig. 5a, a cartoon of a 'typical'-looking microstate is shown, in which the N particles are distributed in a rather disorderly manner within the box, and their velocities also appear randomly distributed. However, the two other microstates pictured in Fig. 5b,c are just as likely as the microstate shown in Fig. 5a, even though they certainly look very special.

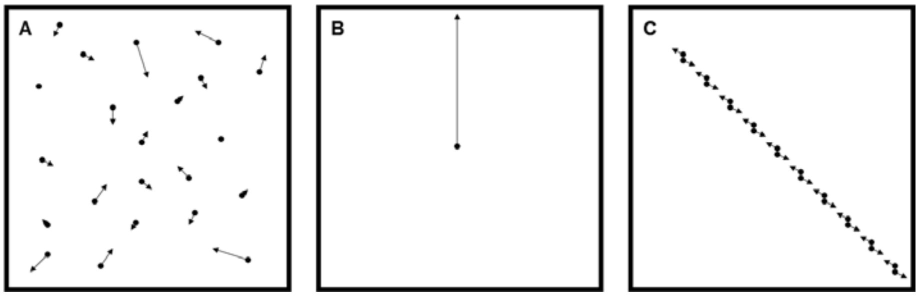

Figure 5: Three equally likely microstates for an ideal gas with N particles in a cubical box of side length L (2D projection shown). (A) A 'typical'-looking microstate, with particles (dots) distributed rather evenly in the box, with random-ish velocities (arrows). (B) Another equally probable microstate, in which all the particles are at the center of the box, and only one has nonzero velocity. (C) Yet another equally probable microstate.

Any particular microstate is completely described by the unique instantaneous list of positions and velocities (or equivalently momenta) of every particle in the box. One way to keep track of this list is to define two very long ($3N$ elements long, to be exact) vectors $\mathbb{R} = (x_1, y_1, z_1, x_2, \ldots x_N, y_N, z_N)$ and $\mathbb{P} = (p_{x1}, p_{y1}, \ldots p_{zN})$. Once these two vectors are defined, the entire microstate is specified. So that means that in order to 'count' the number of available microstates, we need only determine the range of possible values that each of these two vectors could take on. To do this, it is useful to attempt to picture each vector in its respective $3N$-dimensional vector space – 'configuration space' for $\mathbb{R}$ and 'momentum space' for $\mathbb{P}$.[2] The next step is to think about the volume in that space that can be accessed by the system. For example, what is the allowed volume in configuration space? Well, each particle could be anywhere within the $L \times L \times L$ box, and there are N particles, so the allowed volume is a cube in $3N$ dimensions (its projection into $3D$ space is shown in Fig. 6). Thus, the allowed volume in configuration space is L^{3N}, or in general for any volume V containing N non-interacting point particles, the available volume in configuration space is $\Omega_{\text{config}} = V^N$. It is important to note that each point in configuration space represents the configuration state of the entire system of N particles.

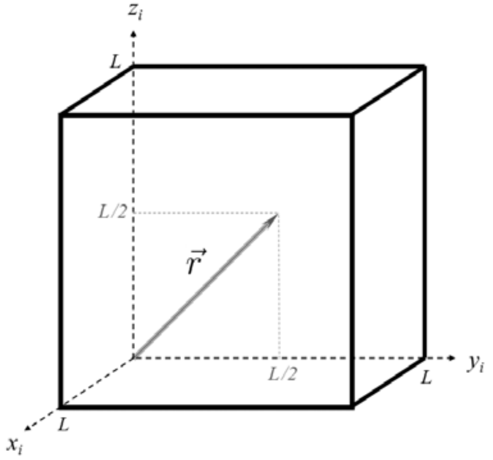

Figure 6: The projection of the available volume in configuration space onto the three spatial dimensions of the ith particle. The projection of one particular microstate is highlighted by the vector $\vec{r} = (\mathbb{R}\cdot\hat{x}_i)\hat{x}_i + (\mathbb{R}\cdot\hat{y}_i)\hat{y}_i + (\mathbb{R}\cdot\hat{z}_i)\hat{z}_i$. In this microstate, the ith particle is located at the position $(0, L/2, L/2)$

Thinking about the available volume in momentum space can be slightly more challenging. The total energy of the system of particles is conserved.

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[2] By the way, the combined $6N$-dimensional space ($\mathbb{R}$,$\mathbb{P}$) is called 'phase space'.

Since there is only kinetic energy, this means that the magnitude of total momentum is also conserved, since $U = \frac{1}{2}mv^2 = p^2/2m$. Thus every allowable point in the $3N$-dimensional momentum space rests on the surface of a $3N$ hypersphere with radius $p = \sqrt{\sum_i \vec{p_i} \cdot \vec{p_i}} = \sqrt{2mU}$ (its projection into $3D$ space is shown in Fig. 7).[3] In other words, the magnitude of $\mathbb{P}$ is fixed at $p = \sqrt{2mU}$, and the direction of $\mathbb{P}$ indicates how that total momentum magnitude is spread out among all $3N$ particle directions.

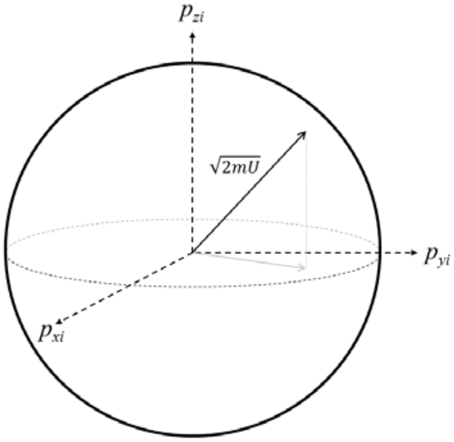

Figure 7: The projection of the available volume in momentum space onto the three momentum dimensions of the ith particle. The projection is a sphere with radius $p = \sqrt{2mU}$.

If we know that the system has total energy U, then the available 'volume' in momentum space is actually just the surface area of a $3N$-dimensional sphere of radius $\sqrt{2mU}$. One convenient way to calculate this surface area is to consider the *volume* of a spherical shell and then divide by its thickness. Taking this approach, we imagine a spherical shell in momentum space that corresponds to a system with total energy between U and $U + dU$. We can compute the volume of this shell by determining the difference in volume between a $3N$-dimensional sphere of radius $\sqrt{2m\,(U + dU)}$ and one of radius $\sqrt{2mU}$. We know that the volume of a sphere with radius R in 3 dimensions is $\frac{4}{3}\pi R^3$. It turns out that the volume of a hypersphere in l dimensions is

$$V(l, R) = \frac{\pi^{l/2} R^l}{(l/2)!}$$

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[3] Mathematicians like to call this kind of spherical surface S_p^{3N-1}, where p is the radius of the sphere in $3N$ dimensions.

Thus the volume V_{shell} of the thin spherical shell in momentum space between U and $U + dU$ is

$$V_{\text{shell}} = V(3N, \sqrt{2m(U + dU)}) - V(3N, \sqrt{2mU})$$

If we divide both sides of the equation by dU, we notice that in the limit $dU \to 0$, the right hand side becomes the derivative $dV(3N, \sqrt{2mU})/dU$:

$$\begin{aligned}
\frac{V_{\text{shell}}}{dU} &= \frac{d}{dU} V(3N, \sqrt{2mU}) \\
&= \frac{d}{dU}\left(\frac{\pi^{\frac{3N}{2}}(2mU)^{\frac{3N}{2}}}{\frac{3N}{2}!}\right) \\
&= \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}(2m)^{\frac{3N}{2}}\left(\frac{3N}{2}\right)U^{\frac{3N}{2}-1} \\
&= \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}\frac{3N}{2U}(2mU)^{\frac{3N}{2}}
\end{aligned}$$

The available volume in momentum space Ω_{mom} is related to this shell volume V_{shell} by

$$V_{\text{shell}} = \Omega_{\text{mom}} dp$$

where dp is the thickness of the shell of radius $p = \sqrt{2mU}$. Thus:

$$\begin{aligned}
\frac{V_{\text{shell}}}{dU} &= \Omega_{\text{mom}} \frac{dp}{dU} \\
&= \Omega_{\text{mom}} \sqrt{\frac{m}{2U}}
\end{aligned}$$

Solving for the available volume in momentum space Ω_{mom}, we find that

$$\Omega_{\text{mom}} = \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}\frac{3N\sqrt{m}}{(2U)^{3/2}}(2mU)^{\frac{3N}{2}}$$

and *finally* we can count the number of available microstates for an ideal gas contained in a volume V with total energy U:

$$\begin{aligned}
\Omega = \Omega_{\text{config}}\Omega_{\text{mom}} &= V^N \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}\frac{3N\sqrt{m}}{(2U)^{3/2}}(2mU)^{\frac{3N}{2}} \\
&\approx V^N \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}(2mU)^{\frac{3N}{2}}
\end{aligned}$$

where we have thrown out the factor of $3N\sqrt{m}(2U)^{-3/2}$ because it is insignificantly small compared with the other factors, which increase exponentially with N.[4] Okay, so now that we have our Ω, we can calculate the entropy $S(U)$:

$$\begin{aligned} S(U) &\approx k_B \ln\left(V^N \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!}(2mU)^{\frac{3N}{2}}\right) \\ &= \frac{3N}{2} k_B \ln(2\pi mU) + Nk_B \ln(V) - k_B \ln\left(\frac{3N}{2}!\right) \end{aligned}$$

and from the entropy we can calculate the temperature T and pressure P:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3Nk_B}{2U} \tag{5}$$

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{Nk_B}{V} \tag{6}$$

The first of the above relations, commonly written as $U/3N = \frac{1}{2}k_BT$, is called the **equipartition theorem**. It states that in an ideal gas, the total energy U is distributed evenly among the $3N$ velocity components, or *degrees of freedom*, with $\frac{1}{2}k_BT$ for each degree of freedom. The second relation, commonly written as $PV = Nk_BT$ is the **Ideal Gas Law**, an example of an *equation of state*.

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[4] If you are worried about throwing away a factor with units, you may be comforted to hear that only *ratios* of Ω are important for typical measurables like probabilities.

6 Chemical potential: Shared particles

Okay, now that we have a microscopic picture of an ideal gas that contains some number N of noninteracting particles that share a fixed total energy U, we can return to other forms of equilibrium. In particular, let's think about an isolated pair of systems that can exchange not only energy but also particles, shown schematically in Fig. 8. The total number of particles $N = N_A + N_B$ and total energy $U = U_A + U_B$ are fixed, but energy and particles may slosh around between the two systems. What happens at equilibrium? By the way, this kind of equilibrium is called 'diffusive' equilibrium, because the the particles are thought to diffuse from one system to the other, perhaps through some permeable membrane.

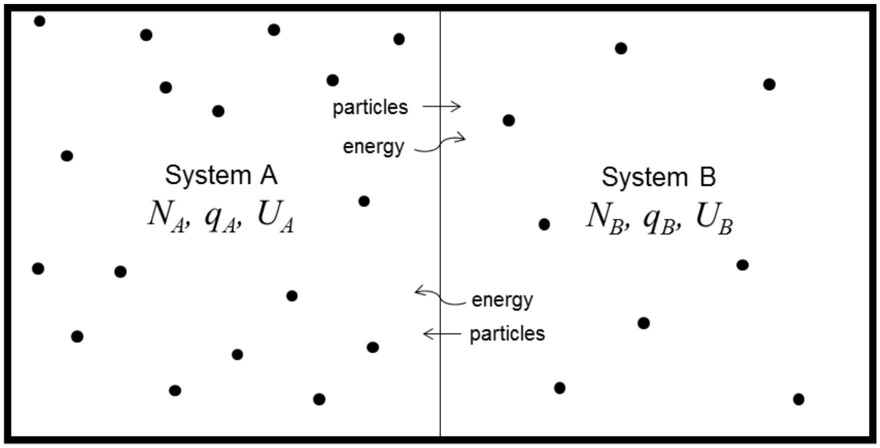

Figure 8: Schematic of two systems A and B that can exchange energy and particles.

We know that at equilibrium, the combined system will be in the most likely macrostate, namely, the macrostate with the highest multiplicity. This corresponds to maximizing the combined multiplicity Ω, or equivalently, maximizing the total entropy $S = k_B \ln \Omega$.[5] In Section 4 we maximized Ω with respect to energy U_A, but here the number of particles N_A can also be varied in addition to the energy U_A. In fact, the total entropy of the combind system is now a function of both U_A and N_A, as depicted in Fig. 9. The most likely macrostate occurs at the values of U_A and N_A that correspond to the highest point on the graph of S.

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[5] If this equivalence isn't obvious, try a fun little math 'proof': Say that $f(x)$ is a positive function so that $f(x) > 0$ for all x, and say that $f(x)$ is maximized at $x = a$. Is the function $g(x) = A \ln f(x)$, where $A > 0$ is a constant, also maximized at $x = a$? Recall what it meas to be at a maximum.

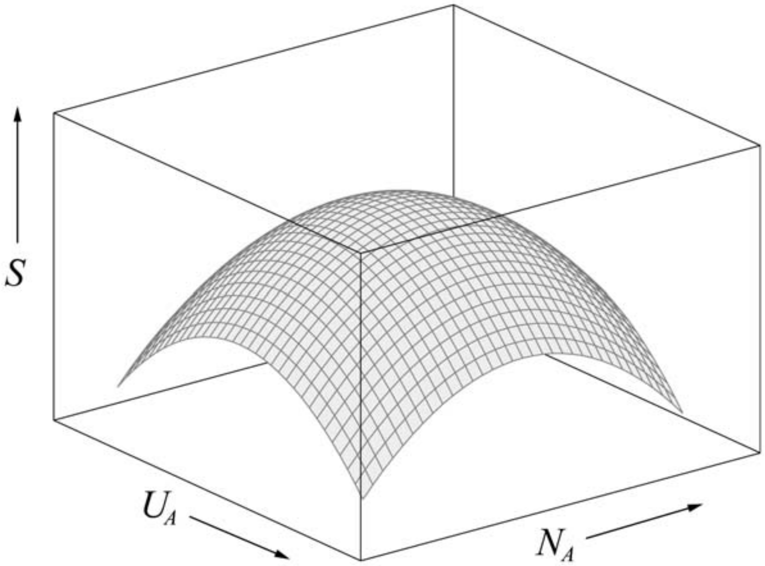

Figure 9: The total entropy S is a function of both the energy in system A and the number of particles in system A.

We can solve for the equilibrium values of U_A and N_A by stating that the entropy S is maximized:

$$\frac{\partial S}{\partial U_A} = 0; \frac{\partial S}{\partial N_A} = 0$$

Here the partial derivatives indicate that in the first condition, N_A and V_A are held fixed, and in the second, U_A and V_A are fixed. We already know that the first condition leads to the statement that $T_A = T_B$. What about the second condition? Since $S = S_A + S_B$,

$$0 = \frac{\partial S}{\partial N_A} = \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_A} = \frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}$$

where in the final step, we have used the fact that $dN_B = -dN_A$ since $N_B = N - N_A$. From this we conclude that at equilibrium,

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

where again we emphasize that U_A and V_A are held fixed for these partial derivatives. Taking advantage of our freedom to multiply both sides by the same factor $-T$, we see that the statement of equilibrium when both energy and particles (but not volume) may be exchanged can be written as

$$-T\left(\frac{\partial S_A}{\partial N_A}\right)_{U,V} = -T\left(\frac{\partial S_B}{\partial N_B}\right)_{U,V}$$
$$\mu_A = \mu_B$$

where we have (*finally*) defined the elusive variable μ as in Equation 4. For some strange reason, the quantity μ is called "chemical potential". It is not a potential energy (although it does have units of energy) and it doesn't describe chemicals *per se*. Like temperature, it is simply the quantity that is equal in equilibrium, for systems that can exchange both energy and particles. That's it.

7 Of systems and reservoirs: Boltzmann statistics

Over the course of this primer, we've gotten pretty good at picturing isolated pairs of systems that are in thermal contact and can exchange some combination of energy, volume, and particles. In each case, we've found a way to quantify the combined multiplicity of both systems and then maximize it by tuning the available thermodynamic variables. How do we think about statistical mechanics or thermodynamics of a single, non-isolated system at equilibrium with its environmental surroundings? For example, say we have an air-filled balloon in a room at 30 C. How do we approach a problem like that? Thankfully, we can just pull out our same trick of considering two systems in contact, but now the two systems are called, rather suggestively, 'system' ($\mathcal{S}$) and 'reservoir' ($\mathcal{R}$). The idea is that the system (balloon) is *much* smaller than the reservoir (defined roughly as everything else in the room: the air, chairs, tables, walls, and so on). A system-reservoir scenario in which energy may be exchanged is depicted in Fig. 10. The total energy $U = U_\mathcal{S} + U_\mathcal{R}$ of the combined system is conserved but can slosh around between the two.

Here's where things get fun. For such a system in thermal contact with a large reservoir, it would be nice to have an expression for the probability $P(s)$ that the system is in a specific microstate s. To tackle that problem, let's start by saying that the system $\mathcal{S}$ is in the exact microstate s with the corresponding energy U_s. In that case, only that one microstate s is available to $\mathcal{S}$, so the multiplicity of the system simply equals one: $\Omega_\mathcal{S} =$

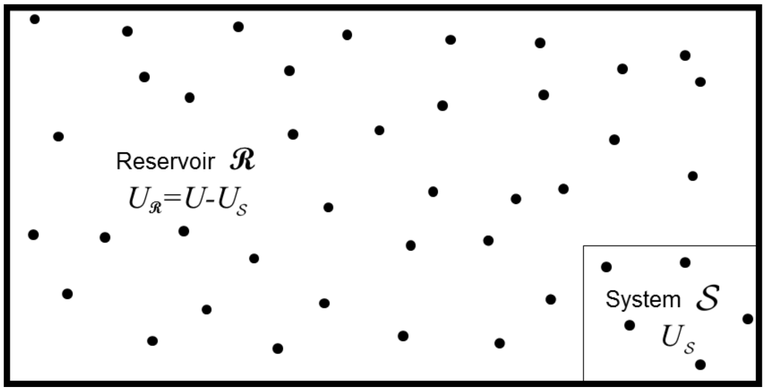

Figure 10: A small system $\mathcal{S}$ and a large reservoir $\mathcal{R}$. Energy may be exchanged between the system and reservoir so that the total energy $U = U_{\mathcal{S}} + U_{\mathcal{R}}$ remains constant.

$\Omega_{\mathcal{S}}(s) = 1$. Furthermore, the total energy remaining for the reservoir is $U_{\mathcal{R}} = U - U_s$. This means that the combined multiplicity of the system and reservoir becomes

$$\begin{aligned}\Omega_{total} &= \Omega_{\mathcal{R}}(U - U_s)\Omega_{\mathcal{S}}(s)\\ &= \Omega_{\mathcal{R}}(U - U_s) \times 1\\ &= \Omega_{\mathcal{R}}(U - U_s)\end{aligned}$$

This means that the combined multiplicity of the system and reservoir is just equal to the multiplicity of the reservoir with its energy slightly reduced by U_s. Using this fact, we can calculate the ratio of the probability $P(s_2)$ that the system is in the specific microstate s_2 with energy U_2 to the probability $P(s_1)$ that it is in microstate s_1 with energy U_1:

$$\begin{aligned}\frac{P(s_2)}{P(s_1)} &= \frac{\Omega_{\mathcal{R}}(U - U_2)}{\Omega_{\mathcal{R}}(U - U_1)}\\ &= \frac{e^{S_{\mathcal{R}}(s_2)/k_B}}{e^{S_{\mathcal{R}}(s_1)/k_B}}\\ &= e^{(S_{\mathcal{R}}(s_2) - S_{\mathcal{R}}(s_1))/k_B}\end{aligned}$$

where we have used the fact that $S = k_B \ln \Omega$. The exponent now contains the change in entropy of the reservoir when the system changes from microstate s_1 to microstate s_2, a *tiny* amount since the system is so much smaller than the reservoir, and since the energy of the system (U_1 or U_2) is very small compared with the total energy U. We are thus free to calculate a first order Taylor series expansion of the form

$$\begin{aligned} S_{\mathcal{R}}(U-\epsilon) &= S_{\mathcal{R}}(U) - \epsilon\left(\frac{\partial S_{\mathcal{R}}}{\partial U_{\mathcal{R}}}\right)_{U_{\mathcal{R}}=U} \\ &= S_{\mathcal{R}}(U) - \frac{\epsilon}{T_{\mathcal{R}}} \\ &= S_{\mathcal{R}}(U) - \frac{\epsilon}{T} \end{aligned}$$

where in the last step we have inserted the equilibrium temperature T of both the system and the reservoir. We can now substitute this approximation back into our expression for the ratio of probabilities of state s_2 and state s_1:

$$\begin{aligned} \frac{P(s_2)}{P(s_1)} &= e^{(S_{\mathcal{R}}(s_2)-S_{\mathcal{R}}(s_1))/k_B} \\ &\approx e^{(S_{\mathcal{R}}(U)-U_2/T-S_{\mathcal{R}}(U)+U_1/T)/k_B} \\ &= e^{-(U_2-U_1)/k_BT} \\ &= \frac{e^{-U_2/k_BT}}{e^{-U_1/k_BT}} \end{aligned}$$

In the last line, we've rewritten then expression as the ratio of two factors of the form $e^{-U(s)/k_BT}$, where $U(s)$ is the energy of the system when it is in the specific microstate s. These are called **Boltzmann factors**, and they are extremely important in statistical mechanics, in fact, so important that we'll repeat it with a numbered equation:

$$\text{Boltzmann factor for state } s = e^{-U(s)/k_BT} \tag{7}$$

So, we are part of the way to getting our expression for $P(s)$; we know the ratio of probabilities $P(s_2)/P(s_1)$, but we need a normalization factor to get the rest of the way there. If we call the normalization factor Z, then the normalization condition is that

$$1 = \sum_s P(s) = \sum_s \frac{e^{-U(s)/k_BT}}{Z} = \frac{1}{Z}\sum_s e^{-U(s)/k_BT}$$

Solving for Z, we find that

$$Z = \sum_s e^{-U(s)/k_BT} \tag{8}$$

This defines the **partition function** Z, a humble normalization constant that will turn out to be one of the most useful statistical quantities. It is, quite simply, the sum of all the Boltzmann factors for every accessible state s available to a system $\mathcal{S}$ in thermal contact with a reservoir $\mathcal{R}$. *Finally,* we obtain our expression for the probability that the system is in the specific microstate s with energy $U(s)$:

$$P(s) = \frac{e^{-U(s)/k_B T}}{Z} \tag{9}$$

This last expression is perhaps the most useful formula in all of statistical mechanics. Memorize it. The probability distribution $P(S)$ is sometimes called the **Bolzmann distribution** or the **canonical distribution**. It is important to remember that it applies to a system in thermal contact with a reservoir where only energy (and not volume or particles) may be exchanged. *Preview*: in systems that can exchange particles in addition to energy, the probability of being in a microstate s is described by the **grand canonical distribution** that involves the **Gibbs factor**, which is similar to the Boltzmann factor.

8 Helmoltz Free Energy

First, some review of what we've learned:

For isolated systems with fixed energy U, the most important statistical quantity is the multiplicty of the system, $\Omega(U)$, the number of available microstates. The logarithm of this is proportional to the entropy $S(U)$, which tends to increase and is maximized in equilibrium (in the thermodynamic limit).

What about a system at equilibrium in contact with a reservoir at temperature T? The quantity most like $\Omega(U)$ is the partition function $Z(T)$, which is roughly equal to the number of microstates available to the system, given that the temperature T (and not the energy U) is fixed. We might therefore guess that the logarithm of Z would be an important quantity like entropy, that tends to increase. However, we physicists love to think about energy, which tends to be minimized, not maximized. We like to picture "energy landscapes" in which the system in question rolls around on a hilly potential energy function and settles into the lowest valley. With this philosophy in mind, we'll now define something called the **Helmholtz free energy**, F:

$$F = U - TS = -k_b T \ln Z \tag{10}$$

Okay, we just pulled that definition out of the blue, and there's a lot going on there. First, the thermodynamic definition: we write the free energy as $F = U - TS$, meaning the energy that is "freely" available if you annihilate a system in equilibrium with a reservoir at temperature T. If an isolated system with energy U were disassembled, then all of its energy would be released and potetially used as work. However, since the system is in contact with a reservoir, some of that energy will get shared as heat with the reservoir, so that the combined mulitplicity of the system plus reservoir is maximized. The amount of heat that will be thus dumped into the reservoir is TS; in other words all of the system's entropy gets lost as heat to the reservoir. Thus only the remaining energy $F = U - TS$ is released as free energy that can be used for work.

Second, the statistical definition: $F = -k_b T \ln Z$. Similar to S, F is proportional to the logarithm of a fundametal statistical quantity. Furthermore, F is minimized in equilibrium. A comparison between S and F in an isolated system at fixed energy U and in a system in contact with a reservoir at fixed temperature T is shown in Fig. 11.

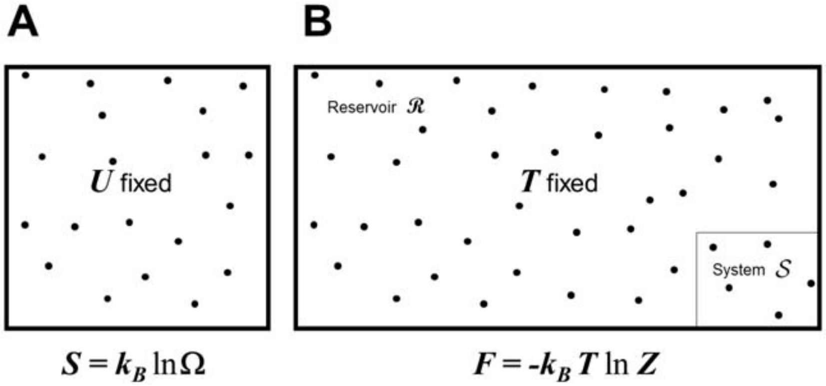

Figure 11: (A) For an isolated system with fixed total energy U, the entropy $S = k_B \ln \Omega$ tends to increase. (B) For a small system $\mathcal{S}$ in thermal equilibrium at temperature T with a large reservoir $\mathcal{R}$, the free energy $F = -k_B T \ln Z$ tends to decrease.

Let's dwell on this Helmholtz free energy a bit longer. It's incredibly important because it connects the microscopic statistical properties of the system to its thermodynamic state. If we can determine the partition function Z, then we can calculate F. It turns out that from F we can compute the entropy, pressure and checmical potential of the system. In practice, in many thermal physics problems, the first step is to determine Z, and then from there calculate the important thermodynamic variables. Below are the three important thermodynamic relations for a system in thermal contact with a reservoir:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \qquad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{11}$$

For each relation, the quantities that are held fixed between the system and reservoir are explicitly identified.

9 The "other" free energies

It is worth noting that there are two other important "free energies" that come up in the literature from time to time.

The first is called the **Gibbs Free Energy**, denoted by G. The Gibbs free energy comes in handy in situations where the system volume is varied at constant pressure. While we won't give G a section of its own, it's worth defining:

$$G = F + pV = U + pV - TS \tag{12}$$

The second is called the Grand Free Energy (or Grand Potential), and it is useful in situations where the number of particles in the system is varied at constant chemical potential. Here is its definition:

$$\Phi = U - TS - \mu N \tag{13}$$

10 Further Reading

- An excellent online resource about partial derivatives in non-Cartesian spaces: http://www.av8n.com/physics/partial-derivative.htm