

PHYS3020 Content Notes

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1 Week 1

1.1 – Thermal Equilibrium

After two objects have been in contact long enough, we say that they are in *thermal equilibrium*. The time required for a system to come to thermal equilibrium is called the *relaxation time*.

There is a second type of equilibrium – *diffusive equilibrium* – in which the molecules of two substances are free to move around but no longer have any tendency to move on way or another. There is also *mechanical equilibrium*, when large-scale motions can take place but no longer do.

Exchanged Quantity	Type of Equilibrium
energy	thermal
volume	mechanical
particles	diffusive

When two objects are able to exchange energy, and energy tends to move spontaneously from one to the other, we say that the object that gives up energy is at a *higher* temperature, and the object that sucks in energy is at a *lower* temperature. With this, we can form a basic theoretical definition of temperature:

Temperature is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously *lose* energy is at the *higher* temperature.

1.2 – The Ideal Gas

Many of the properties of a low-density gas can be summarized in the *ideal gas law*

$$PV = nRT \quad (1.1)$$

where P is pressure, V volume, n number of moles of gas, R Rydberg's constant, and T is the temperature in K. There are some useful constants in the table below

Constant	Value	Units
Rydberg Constant	8.31	J/mol/K
Mole = N_A	6.02×10^{23}	
Boltzmann's Constant	1.381×10^{-23}	J/K
Atmosphere	101.3	kPa
Electron Volt	1.6×10^{-19}	J/eV

The number of molecules in an amount of substance is denoted by a capital N , such that

$$N = n \times N_A \implies nR = Nk \quad (1.4 \text{ \& } 1.7)$$

Microscopic Model of an Ideal Gas

For each dimension of movement for a particle,

$$kT = m\overline{v_x^2} \quad \text{or} \quad \overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT \quad (1.15)$$

In the above I used x as the direction, but it also holds for y and z such that the translational kinetic energy of a particle is

$$\overline{K}_{\text{trans}} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m \left(\overline{v_x^2 + v_y^2 + v_z^2} \right) = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \quad (1.17)$$

The root-mean-square of 3-dimensional particle movement (which is only slightly larger than the particle's velocity magnitude) is

$$v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \quad (1.21)$$

The ideal gas law breaks down when the density gets too high; the model relies on an underlying assumption that molecules spend most of their time travelling in straight lines and not interacting with boundaries or other particles.

1.3 – Equipartition of Energy

Equation (1.17) is a special case of a much more general result, called the **equipartition theorem**. Each form of energy (that is a quadratic function of a coordinate or velocity component) is called a *degree of freedom*.

Equipartition theorem: At temperature T , the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$.

If a system contains N molecules, each with f degrees of freedom, and there are no other (non-quadratic) temperature-dependent forms of energy, then its *total* thermal energy is

$$U_{\text{thermal}} = N \cdot f \cdot \frac{1}{2}kT \quad (1.23)$$

This is just an average total of the thermal energy, but for large N this is close to the true value.

The quantity U_{thermal} is almost never the *total* energy of the system (it doesn't account for static energy like in rest mass-energy or chemical bonds, etc), and so it is safest to apply the above only to changes in energy when the temperature is raised or lowered (when there are no phase transitions!).

In a gas of monatomic molecules like helium or argon, only translational motion contributes to the number of degrees of freedom (so each molecule has three degrees of freedom). In a diatomic gas, like O_2 , each molecule can also *rotate* about two different axes (the third axis is symmetric and doesn't count). A diatomic molecule can also *vibrate*, as if the two atoms were held together by a spring. This counts as two degrees of freedom, one for the vibrational kinetic energy and one for the potential energy. Each “mode” of vibration counts as two degrees of freedom.

However, at room temperature many vibrational degrees of freedom don't contribute to a molecule's thermal energy. So, for example, air molecules only have 5 DoF at room temperature and not 7. At higher temperatures, the vibrational modes do eventually contribute and we say that these modes are “frozen out” at room temperature.

In a solid, each atom can vibrate in three perpendicular directions, so for each atom there are six degrees of freedom (three for kinetic and three for potential energy).

1.4 – Heat and Work

While energy can often be converted from one form to another, the total amount of energy in the universe never changes. This is the famous law of **conservation of energy**. There are all sorts of mechanisms by which energy can be put into or taken out of a system. In the context of thermodynamics, this is usually classified under **heat** and **work**.

Heat is defined as any spontaneous flow of energy from one object to another, caused by a difference in temperature between the objects. We say that heat flows from one object to another.

Work, in thermodynamics, is defined as any other transfer of energy into or out of a system. Usually with work, we can identify some “agent” that is “actively” putting energy into the system; it wouldn't happen “automatically”.

Heat and work refer to energy *in transit*. A system contains energy, but it does not contain heat or work.

A change of energy in a system, ΔU , can be expressed in terms of a sum of the heat and work, Q and W respectively, that enter the system:

$$\Delta U = Q + W \quad (1.24)$$

The above is generally called the **first law of thermodynamics**.

2.1 – Two-State Systems

In general, to specify the *microstate* of a system, we must specify the state of each individual particle. If we specify the state of a system more generally (e.g. just by saying how much of some parameter there is [as opposed to the exact value of each particle’s parameter]), we call it a *macrostate*. If you know the microstate of a system, then you know the macrostate too! This does not hold the other way around, though. The number of microstates corresponding to a given macrostate is called the *multiplicity*, Ω , of that macrostate.

The probability of any particular macrostate (for counting the number of successes of a test) can be written

$$\text{probability of } n \text{ successes} = \frac{\Omega(n)}{\Omega(\text{all})} \quad (2.1)$$

If there are N “particles”, the multiplicity of the macrostate with n “successes” is

$$\Omega(N, n) = \frac{N!}{n! \cdot (N - n)!} = \binom{N}{n} \quad (2.6)$$

This is the number of ways of choosing n objects out of N .

The Two-State Paramagnet

A *paramagnet* is a material in which the constituent particles act like tiny compass needles that tend to align *parallel* to any externally applied magnetic field. The individual magnetic particles can be referred to as *dipoles*, because each has its own magnetic dipole moment vector. Due to quantum mechanics, only certain discrete values for the dipole moment vector are allowed. In the simplest case, only two values are allowed, one positive and the other negative. We then have a *two-state paramagnet*, in which each elementary compass needle can have only two possible orientations, either parallel or antiparallel to the applied field.

Let’s define N_\uparrow to be the number of elementary dipoles that point up (at some particular time), and N_\downarrow to be the number of dipoles that point down. The total number of dipoles is then $N = N_\uparrow + N_\downarrow$. This system has one macrostate for each possible value of N_\uparrow , from 0 to N . The multiplicity of any macrostate is given by the same formula as above:

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \quad (2.7)$$

The external magnetic field exerts a torque on each dipole, trying to twist it to point parallel to the field. If the external field points up, then an up-dipole has *less* energy than a down-dipole, since you would have add energy to twist it from up to down. The total energy of the system is determined by the total numbers of up- and down-dipoles, so specifying which macrostate the system is in is the same as specifying its total energy.

2.2 – The Einstein Model of a Solid

Consider a collection of microscopic systems that can each store any number of energy “units”, all of the same size. Equal-size energy units occur for any quantum-mechanical *harmonic oscillator*, whose potential energy function has the form $\frac{1}{2}k_s x^2$ (where k_s is the “spring constant”). The size of the energy units is then hf , where h is Planck’s constant (6.63×10^{-34} J.s), and f is the natural frequency of the oscillator ($\frac{1}{2\pi} \sqrt{k_s/m}$).

In a three-dimensional solid, each atom can oscillate in three independent directions, so if there are N oscillators, there are only $N/3$ atoms. This is an *Einstein solid*. The general formula for the multiplicity of an Einstein solid with N oscillators and q energy units is

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \quad (2.9)$$

2.3 – Interacting Systems

Let’s assume that, over long time scales, the energy gets passed around randomly in such a way that all microstates are equally probably. So, if you look at the system at any instant, you are equally likely to find it in any of the microstates. This assumption is called the *fundamental assumption of statistical mechanics*:

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

At the microscopic level, we expect that any process that would take the system from state X to state Y is reversible, so that the system can just as easily go from state Y to state X . For a large system, the number of “accessible” microstates is usually so huge that only a minuscule fraction of them could possibly occur within a lifetime.

For a system of two solids, the total multiplicity of any macrostate is the product of the multiplicities of the individual solids (if they are independent of each other).

All microstates are equally probable, but some *macrostates* are more probable than others. If all of the energy is in one solid initially, after waiting a while it's very likely that the energy will be more evenly distributed. In fact, the macrostates with the most evenly distributed energies are the most likely (given enough time has passed for energy to evenly distribute).

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}
...
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}
...
100	1.7×10^{96}	0	1	1.7×10^{96}
				9.3×10^{115}

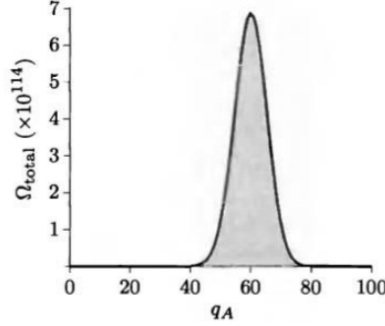


Figure 1: Macrostates and multiplicities of a system of two Einstein solids, with 300 and 200 oscillators respectively, sharing a total of 100 units of energy.

Suppose that this system is *initially* in a state with q_A much less than 60; perhaps all of the energy starts out in solid B . After waiting a while to allow the energy to rearrange itself, you are more or less certain to find that energy has flowed from B to A . This system exhibits *irreversible* behaviour: energy flows spontaneously from B to A , but never (aside from small fluctuations around $q_A = 60$) from A to B . This is a physical explanation of *heat*: it is a *probabilistic* phenomenon; not absolutely certain, but extremely likely.

The spontaneous flow of energy *stops* when a system is at, or very near, its most likely macrostate (the macrostate with the greatest multiplicity). This is one version of the **second law of thermodynamics**.

2.4 – Large Systems

For systems of a larger number of components (or particles), the multiplicity function becomes much sharper. That is, the width of the distribution in Figure 2.5 gets smaller and the peak steeper and so only a tiny fraction of all possible macrostates are reasonably probable.

Stirling's Approximation

Formulas for multiplicities involve combinations which involve factorials. To apply these to large systems, we need an approximation for large numbers which ordinarily can't be computed: *Stirling's approximation*:

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \quad (2.14)$$

which is accurate in the limit where $N \gg 1$.

Multiplicity of a Large Einstein Solid

First, consider only the case $q \gg N$, when there are many more energy units than oscillators (this is the “high-temperature” limit). Then,

$$\Omega(N, q) \approx e^{N \ln(q/N)} e^N \left(\frac{eq}{N}\right)^N \quad (2.21)$$

Sharpness of the Multiplicity Function

For some system of N components and q energy units, it will have a very sharp peak at $q_A = q/2$, where the energy is distributed equally between two solids. The height of this peak is a very large number

$$\Omega_{\text{max}} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} \quad (2.23)$$

To find the multiplicity, near the peak for some $x \ll q$,

$$\Omega = \left(\frac{e}{N}\right)^{2N} e^{N \ln(q/2)^2} e^{-N(2x/q)^2} = \Omega_{\text{max}} \cdot e^{-N(2x/q)^2} \quad (2.27)$$

A function of this form is called a **Gaussian**; it has a peak at $x = 0$ and a sharp fall-off on either side. The multiplicity falls off to $1/e$ of its maximum value when

$$N \left(\frac{2x}{q} \right)^2 = 1 \quad \text{or} \quad x = \frac{q}{2\sqrt{N}} \quad (2.28)$$

This says that, if $N \sim 10^{20}$, and the width of the peak is given by 1cm, the full scale of the graph would be on the order of 100,000km. This result tells us that, when two large Einstein solids are in thermal equilibrium with each other, any random fluctuations away from the most likely macrostate will be *utterly immeasurable*. The limit where a system becomes infinitely large, so that fluctuations away from the most likely macrostate never occur, is called the *thermodynamic limit*.

2.5 – The Ideal Gas

The conclusion that only a *tiny* fraction of the macrostates of a large interacting system have reasonably large probabilities applies to essentially any pair of interacting objects, provided that the number of particles and the number of energy units are both “large”.

Multiplicity of a Monatomic Ideal Gas

Suppose we have a single gas atom, with total energy U , in a container of volume V . A container with twice the volume offers twice as many states to a molecule, so the multiplicity should be proportional to V . Also, the more different momentum vectors the molecule can have, the more states are available, so the multiplicity should also be proportional to the “volume” of available **momentum space** – momentum space is an imaginary space in which the axes are p_x , p_y , and p_z ; each “point” in momentum space corresponds to a momentum vector for the particle. So,

$$\Omega_1 \propto V \cdot V_p \quad (2.29)$$

where V is the volume of ordinary space (**position space**), V_p is the volume of momentum space, and the 1 subscript indicates that this is for a gas of just one molecule.

One problem is in determining the available volume of momentum space. Since the molecule’s kinetic energy must equal U , there is a constraint:

$$U = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \quad (2.30)$$

The above equation can also be written as $p_x^2 + p_y^2 + p_z^2 = 2mU$, which defines the surface of a sphere in momentum space with radius $\sqrt{2mU}$. The “volume” of momentum space is really the *surface area* of this sphere.

To actually count the number of microstates we must invoke quantum mechanics. The less spread out a wavefunction of a particle is in position space, the more spread out it must be in momentum space, and vice versa. This is the **Heisenberg uncertainty principle**:

$$(\Delta x)(\Delta p_x) \approx h \quad (2.32)$$

In this one-dimensional example, the number of (finite) distinct position states is $L/(\Delta x)$, while the number of distinct momentum states is $L_p/(\Delta p_x)$. The total number of distinct states is the product,

$$\frac{L}{\Delta x} \frac{L_p}{\Delta p_x} = \frac{LL_p}{h} \quad (2.33)$$

Where L is the length of position space, etc. In three dimensions, the lengths become volumes and there are three factors of h :

$$\Omega_1 = \frac{V V_p}{h^3} \quad (2.34)$$

All so far has only been for a gas of one molecule. If we add a second molecule, we need a factor of the form of equation (2.34) for each molecule. The V_p factors get more complicated, since only the *total* energy of the two molecules is constrained: $p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = 2mU$, assuming that both molecules have the same mass. This equation defines the surface of a 6-dimensional “hypersphere” in six-dimensional momentum space. So, the multiplicity function for an ideal gas of two molecules should be

$$\Omega_2 = \frac{V^2}{h^6} \times (\text{area of momentum hypersphere}) \quad (2.36)$$

This formula is correct only if the two molecules are distinguishable from one another. If they are indistinguishable, then the microstates have been overcounted by a factor of two and so

$$\Omega_2 = \frac{1}{2} \frac{V^2}{h^6} \times (\text{area of momentum hypersphere}) \quad (2.37)$$

For an ideal gas of N indistinguishable molecules, the multiplicity function contains N factors of V , divided by $3N$ factors of h , with overcounting of a factor of $1/N!$:

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times (\text{area of momentum hypersphere}) \quad (2.38)$$

Where the surface area of a d -dimensional hypersphere is

$$\text{“area”} = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!} r^{d-1} \quad (2.39)$$

Finally, we obtain

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} (\sqrt{2mU})^{3N-1} \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N} \quad (2.40)$$

This formula is messy, but its dependence on U and V is simple:

$$\Omega(U, V, N) = f(N) V^N U^{3N/2} \quad (2.41)$$

where $f(N)$ is a complicated function of N .

For any system with only quadratic “degrees of freedom”, having so many units of energy that energy quantization is unnoticeable, the multiplicity is proportional to $U^{Nf/2}$, where Nf is the total number of degrees of freedom.

Interacting Ideal Gases

Suppose now that we have two ideal gases, separated by a partition that allows energy to pass through. If each gas has N molecules (of the same species), then the total multiplicity of the system is

$$\Omega_{\text{total}} = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2} \quad (2.42)$$

The multiplicity function will have a very sharp peak:

$$\text{width of peak} = \frac{U_{\text{total}}}{\sqrt{3N/2}} \quad (2.43)$$

Provided that N is large, only a *tiny* fraction of the macrostates will have a reasonable chance of occurring, assuming that the system is in equilibrium.

In addition to exchanging energy, we could allow the gases to exchange volume by allowing the partition to move back and forth as one gas expands and the other contracts. The multiplicity, plotted as a function of V_A , again has a very sharp peak:

$$\text{width of peak} = \frac{V_{\text{total}}}{\sqrt{N}} \quad (2.44)$$

So again, the equilibrium macrostate is essentially determined, to within a tiny fraction of the total volume available (if N is large).

2 Week 2

2.6 – Entropy

Any large system in equilibrium will be found in the macrostate with the greatest multiplicity (aside from fluctuations that are normally too small to measure). This is a more general statement of the **second law of thermodynamics**. Another way to say it is simply: *multiplicity tends to increase*.

Since multiplicities tend to be very large numbers, it’s convenient to work with the natural logarithm of the multiplicity, with a factor of Boltzmann’s constant applied in what we call **entropy**:

$$S \equiv k \ln \Omega \quad (2.45)$$

Generally, the more particles that are in a system and/or the more energy it contains, the greater its multiplicity and its entropy. Besides adding particles and energy, you can increase the entropy of a system by letting it expand into a larger space, or breaking large molecules apart into small ones, or mixing together substances that were once separate. In all of these cases, the total number of possible arrangements increases.

The total entropy of a composite system is the *sum* of the entropies of its parts:

$$S_{\text{total}} = k \ln \Omega_{\text{total}} = k \ln(\Omega_A \Omega_B) = k \ln \Omega_A + k \ln \Omega_B = S_A + S_B \quad (2.48)$$

We can restate the *second law of thermodynamics* as

Any large system in equilibrium will be found in the macrostate with the greatest entropy (aside from negligible fluctuations).

Or, more briefly: *entropy tends to increase*.

Entropy of an Ideal Gas

If you start with equation (2.40), apply Stirling's approximation, and throw away some factors that are merely large (as opposed to very large), and take the logarithm, you get

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3NH^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (2.49)$$

This is known as the **Sackur-Tetrode equation**.

The entropy of an ideal gas depends on its volume, energy, and number of particles. Increasing any of these three variables increases the entropy. The simplest dependence is on the volume; if the volume changes from V_i to V_f while U and N are held fixed, the entropy changes by

$$\Delta S = Nk \ln \left(\frac{V_f}{V_i} \right) \quad (2.51)$$

Another way of changing the volume of a gas is by **free expansion**, where the molecules of a gas expand to fill a container that they're in. No heat or work is done in this process, since there is no external influence on the gas, and so, for *free expansion*, $\Delta U = Q + W = 0 + 0 = 0$.

Entropy of Mixing

Another way of creating entropy is by letting two different materials mix with each other. Suppose we have two different monatomic ideal gases, each with the same parameters but are separated by a partition. When the partition is lifted, each gas expands to fill twice its initial volume. And so

$$\Delta S_A = Nk \ln \left(\frac{V_f}{V_i} \right) = Nk \ln \left(\frac{2V_i}{V_i} \right) = 2Nk \ln 2 \quad (2.53)$$

Since the entropy of both gases increase by the same amount,

$$\Delta S_{\text{total}} = \Delta S_A + \Delta S_B = 2Nk \ln 2 \quad (2.54)$$

This increase is called the **entropy of mixing**, but it's important to note that this result only holds for two *different* gases with the same parameters that expand to twice their initial volume. If the same gas is on both sides (with identical parameters), there will be no entropy increase.

Reversible and Irreversible Processes

If a physical process increases the total entropy of the universe, that process cannot happen in reverse, since this would violate the second law of thermodynamics. Processes that create new entropy are therefore called **irreversible**. By the same token, a process that leaves the total entropy of the universe unchanged would be **reversible**.

One type of process that creates new entropy is the very sudden expansion of a system, but a gradual expansion, or **quasistatic** volume change doesn't (by itself) change the entropy of the system and is reversible.

Heat flow is always irreversible, however the increase in entropy becomes negligible in the limit where the temperature difference between two objects goes to zero.

Reversible processes can be defined as ones that can be reversed by changing the conditions only infinitesimally.

3.1 – Temperature

Consider two Einstein solids, A and B that can exchange energy (with total energy, U_{total} , fixed). The equilibrium state of the system (at most likely macrostate) is when

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad \text{at equilibrium} \quad (3.3)$$

In other words, the thing that's the same for both systems when they're in thermal equilibrium is the *slope* of their entropy vs energy graphs. The second law tells us that energy will always tend to flow *into* the object with the *steeper* S vs U curve, and *out* of the object with the *shallower* S vs U graph. The former wants to gain energy to increase its entropy, and the latter doesn't mind losing a little bit of energy to increase the total entropy. A steep slope corresponds to a low temperature, and vice versa.

The **temperature** of a system is the reciprocal of the slope of its entropy vs energy graph. The partial derivative is to be taken with the system's volume and number of particles held fixed; more explicitly:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N, V} \quad (3.5)$$

3.2 – Entropy and Heat

Predicting Heat Capacities

The heat capacity at a constant volume (or “energy capacity”) is

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N, V} \quad (3.14)$$

Utilising equation (1.23) [$U = \frac{1}{2}NfkT$], we get

$$C_V = \frac{\partial}{\partial T} \left(\frac{1}{2}NfkT \right) = \frac{1}{2}Nfk \quad (3.15 \text{ \& } 3.16)$$

Measuring Entropies

According to the theoretical definition of temperature (3.5), if you add a bit of heat Q to a system while holding its volume constant and doing no other forms of work, its entropy changes by

$$dS = \frac{dU}{T} = \frac{Q}{T} \quad (\text{constant volume, no work}) \quad (3.17)$$

This also holds when the volume is changing, provided that the process is quasistatic. To get the change in entropy over a non-negligible change in temperature,

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT \quad (3.19)$$

Over small enough temperature change, C_V is usually fairly constant and so can be taken out of the integral.

At zero temperature, a system should settle into its unique lowest-energy state, so $\Omega = 1$ and $S = 0$. This fact is often called the **third law of thermodynamics**. Often, however, there will remain some **residual entropy** according to the arrangement of crystalline structure of a solid at absolute zero, equal to k times the logarithm of the number of possible molecular arrangements. If C_V is known all the way down to absolute zero, a system's *total* entropy is

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T} dT \quad (3.21)$$

This does appear to diverge at its lower limit, and if it did so, either S_f would be infinity or $S(0)$ would be negative infinity. Entropy, however, must always be finite and positive so the only way out is if C_V goes to zero at $T = 0$:

$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 \quad (3.22)$$

This result is also sometimes called the **third law of thermodynamics**.

3.3 – Paramagnetism

Notation and Microscopic Physics

Take a system consisting of N spin-1/2 particles, immersed in a constant magnetic field \vec{B} pointing in the $+z$ direction. Each particle behaves like a little compass needle, feeling a torque that tries to align its magnetic dipole moment with the field, and so the particles can be referred to as **dipoles**. Assume that this system is an **ideal paramagnet** in that each dipole feels only the torque from the external field. The magnetic field, pointing in the $+z$ direction, gives each dipole a preference for the *up* state. To flip a single dipole from up to down, we would have to add energy; the amount of energy required is $2\mu B$, where μ is a constant related to the particle's magnetic moment. The energy of a dipole that points up is $-\mu B$, so that the energy of a dipole that points down is $+\mu B$. The total energy of the system is then

$$U = \mu B(N_{\downarrow} - N_{\uparrow}) = \mu B(N - 2N_{\uparrow}) \quad (3.25)$$

where N_{\uparrow} and N_{\downarrow} are the numbers of up and down dipoles, respectively, and $N = N_{\uparrow} + N_{\downarrow}$. The **magnetization**, M , is defined to be the total magnetic moment of the whole system, such that each “up” dipole has magnetic moment $+\mu$ and each “down” magnetic dipole has moment $-\mu$. So,

$$M = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B} \quad (3.26)$$

The multiplicity of the system is then simply

$$\Omega(N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} \quad (3.27)$$

Numerical Solution

For small systems, (3.27) can just be computed directly. Interestingly, the largest multiplicity and largest entropy occur at $U = 0$ when exactly half of the dipoles point down/up. As more energy is added to the system, the multiplicity and entropy actually *decrease*, since there are fewer ways to arrange the entropy.

Suppose the system starts out in its minimum-energy state (all of the dipoles pointing up). The slope of the entropy-energy graph is very steep so the system has a strong tendency to absorb energy from its environment. As the energy of the paramagnet goes to zero, so does the slope of its entropy-energy graph, so its tendency to absorb more energy actually disappears. At this point, exactly half of the dipoles point down. If we now add more energy to the system, the slope of its entropy-energy graph becomes negative so it will spontaneously give up energy to any nearby object whose entropy-energy graph has a positive slope.

Analytic Solution

Assuming that the number of elementary dipoles is large, equation (3.27) can be simplified with Stirling’s approximation:

$$\begin{aligned} S/k &= \ln N! - \ln N_{\uparrow}! - \ln(N - N_{\uparrow})! \\ &\approx N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow}) \end{aligned} \quad (3.28)$$

The temperature is then

$$\frac{1}{T} = \frac{k}{2\mu B} \ln \left(\frac{N - U/\mu B}{N + U/\mu B} \right) \quad (3.30)$$

This equation can be solved for U to obtain

$$U = -N\mu B \tanh \left(\frac{\mu B}{kT} \right) \quad (3.31)$$

The magnetization is therefore

$$M = N\mu \tanh \left(\frac{\mu B}{kT} \right) \quad (3.32)$$

At very small temperatures, the system is completely magnetized, while as $T \rightarrow \infty$, the magnetization goes to zero. To obtain a negative temperature, the system need only be given a negative magnetization.

To obtain the heat capacity of a paramagnet, equation (3.31) must be differentiated with respect to T ,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N, B} = Nk \cdot \frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)} \quad (3.33)$$

which approaches zero at both low and high T .

In a real-world paramagnet, electronic paramagnetism occurs when there are electrons with angular momentum (orbital or spin) that is not compensated by other electrons; the circular currents then give rise to magnetic dipole moments.

3 Week 3

4 Week 4

6.1 – The Boltzmann Factor

This section introduces a powerful tool in statistical mechanics: a formula of the probability of finding a system in any particular microstate, when that system is in thermal equilibrium with a “reservoir” at a specified temperature. The

system can be almost anything, but let's say that it's a single atom.

In this case, the microstates of the system then correspond to the various energy levels of the atom, although for a given energy level there is often more than one independent state (e.g. a hydrogen atom has only one ground state, but 4 independent states on the first energy level, 9 on the second, etc). When an energy level corresponds to more than one independent state, we say that level is **degenerate**.

Now, take two atoms in a 'reservoir' – a system isolated from the rest of the universe. If one atom is in state s_1 , then the reservoir will have some very large number of accessible states, $\Omega_R(s_1)$ – the multiplicity of the *reservoir* when the atom is in state s_1 , all equally probable. Similarly, if an atom is in a state s_2 , the multiplicity of the reservoir is $\Omega_R(s_2)$. These two multiplicities will generally be different, because when the atom is in a lower-energy state, more energy is left for the reservoir and so it will have a larger multiplicity.

The probability of finding the atom in any particular state is directly proportional to the number of microstates that are accessible to the reservoir. The ratio of probabilities for any two states is

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} \quad (6.1)$$

Alternatively, when the energy of each state is known,

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = e^{-(E(s_2)-E(s_1))/kT} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}} \quad (6.5)$$

The ratio of probabilities is equal to a ratio of simple exponential factors, each of which is a function of the energy of the corresponding microstate and the temperature of the reservoir. Each of these exponential factors is called a **Boltzmann factor**:

$$\text{Boltzmann factor} = e^{-E(s)/kT} \quad (6.6)$$

There exists a constant of proportionality that converts a Boltzmann factor into a probability: $1/Z$. This separates the dependence of the probability of one state relying on the probability of another, such that

$$\mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT} \quad (6.8)$$

Equation (6.8) is often called the **Boltzmann distribution** or the **canonical distribution**.

In atomic systems (at the very least), the ground state will have the highest probability, and the remaining states have probabilities proportional to how their energies compare to kT .

The Partition Function

Recall that the probability of an atom being in *some* state must be one, and so the sum of all of the states will allow the calculation of Z ,

$$Z = \sum_s e^{-E(s)/kT} = \text{sum of all Boltzmann factors} \quad (6.10)$$

Often systems will have an infinite family of possible states, but usually their probability approaches 0 as E_s gets larger. In practice, therefore, only the first several terms need only be accounted for to get an approximate solution.

The quantity Z is called the **partition function**, and doesn't depend on any state but *does* depend on temperature.

The thermal average energy of the system is

$$U = \langle E \rangle = \sum_s E_s \mathcal{P}(s) = \frac{1}{Z} \sum_s E_s e^{-E(s)/kT} \quad (6.17)$$

3.4 – Mechanical Equilibrium and Pressure

Consider two systems (gases) separated by a movable partition, which are free to exchange both energy and volume, but the total energy and volume are fixed. At equilibrium (with energy and number of particles held fixed),

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad \text{at equilibrium} \quad (3.38)$$

The relationship between entropy and pressure is also given by

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U,N} \quad (3.39)$$

The Thermodynamic Identity

The thermodynamic identity summarizes both the theoretical definition of temperature and equation (3.39)s formula for pressure:

$$dU = T dS - P dV \quad (3.46)$$

This equation is true for any infinitesimal change in any system, provided that T and P are well defined and no other relevant variables are changing.

Entropy and Heat Revisited

It is tempting to associate the thermodynamic identity with the first law of thermodynamics, $dU = Q + W$. Such an association is only valid in the case of a quasistatic process (where the pressure is always uniform throughout the system):

$$Q = T dS \quad (\text{quasistatic}) \quad (3.48)$$

Under these conditions, the change in a system's entropy is Q/T , even if work is being done on it during the process. In the special case of an adiabatic process ($Q = 0$) that is also quasistatic, the entropy is unchanged; such a process is called *isentropic*.

For constant-pressure processes in which the temperature changes, we can write $Q = C_P dT$, then integrate to obtain

$$(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T} dT \quad (3.50)$$

5.1 – Free Energy as Available Work

The *enthalpy* of a system is its energy plus the work needed to make room for it, in an environment with constant pressure P :

$$H \equiv U + PV \quad (5.1)$$

This is the total energy you would need to create a system out of nothing and put it in such an environment. Or, if you could completely annihilate a system, H is the energy you could recover: the system's energy plus the work done by the collapsing atmosphere.

If the environment is one of constant temperature, the system can extract heat from this environment for free, so all we need to provide, to create the system from nothing, is any additional *work* needed.

One useful quantity is the *Helmholtz free energy*,

$$F \equiv U - TS \quad (5.2)$$

which is the total energy needed to create the system, minus the heat you can get for free from an environment at temperature T . F is the energy that must be provided as work if you're creating a system out of nothing.

If a system is in an environment with constant pressure P and constant temperature T , then the work *you* need to do to create it, or the work you can recover when you destroy it, is given by the *Gibbs free energy*,

$$G \equiv U - TS + PV \quad (5.3)$$

Usually we look at processes that are much less dramatic than the creation or annihilation of entire systems, and so we want to look at the change in the quantities F and G instead.

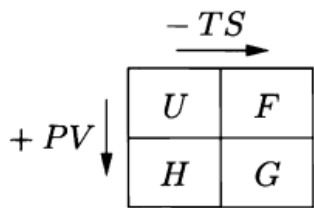


Figure 5.2: To get H from U or G from F , add PV ; to get F from U or G from H , subtract TS .

The four functions U , H , F , and G are collectively called *thermodynamic potentials*.

For any change in the system that takes place at constant temperature T , the change in F is

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S \quad (5.4)$$

where Q is the heat added and W is the work done on the system. If no *new* entropy is created during the process, then $Q = T\Delta S$, so the change in F is precisely equal to the work done on the system. If new entropy *is* created, then $T\Delta S$ will be greater than Q , so

$$\Delta F \leq W \quad \text{at constant } T \quad (5.5)$$

If the environment is one of constant pressure, and if we're not interested in keeping track of the work that the environment does automatically, then we should think about G instead of F . For any change that takes place at constant T and P ,

$$\Delta G = \Delta U - T\Delta S + P\Delta S = Q + W - T\Delta S + P\Delta V \quad (5.6)$$

The difference $Q - T\Delta S$ is always zero or negative. Meanwhile, W includes the work done by the environment, $-P\Delta V$, plus any "other" work done on the system: $W = -P\Delta V + W_{\text{other}}$. This $P\Delta V$ cancels the one in equation (5.6), leaving

$$\Delta G \leq W_{\text{other}} \quad \text{at constant } T, P \quad (5.8)$$

One last useful formula is

$$\Delta G = \Delta H - T\Delta S \quad (5.9)$$

Thermodynamic Identities

If you're given the enthalpy or free energy of a substance under one set of conditions, but need to know its value under some other conditions, there are some handy formulas that are often useful. These formulas resemble the thermodynamic identity [equation (3.46)], but are written for H , F , or G instead of U ,

$$dU = T dS - P dP + \mu dN \quad (5.16)$$

(where μ is the chemical potential).

The thermodynamic identity for H tells you how H changes as you change the entropy, pressure and/or number of particles:

$$dH = T dS + V dP + \mu dN \quad (5.18)$$

Similarly for F and G ,

$$dF = -S dT - P dV + \mu dN \quad (5.20)$$

$$dG = -S dT + V dP + \mu dN \quad (5.23)$$

In all of these formulas, it is implicitly assumed that the system contains only one type of particle. If it is a mixture of several types, then the μdN terms needs to be replaced with $\sum \mu_i dN_i$ in every thermodynamic identity.

5.2 – Free Energy as a Force toward Equilibrium

For an *isolated* system, the entropy tends to increase; the system's entropy is what governs the direction of spontaneous change. But, if the system is in good thermal contact with its environment, energy can pass between the system and the environment and the thing that tends to increase is not the *system's* entropy but rather the *total* entropy (of the system plus environment).

It's useful to approximate the environment as a "reservoir" of energy, large enough that it can absorb and release unlimited amounts of energy without changing its temperature. The fundamental rule is that the total entropy of the universe tends to increase, so let's consider a small change in the total entropy:

$$dS_{\text{total}} = dS + dS_R \quad (5.26)$$

where S denotes the entropy of the system and S_R denotes the entropy of the reservoir. Under the conditions of fixed T , V , and N ,

$$dS_{\text{total}} = -\frac{1}{T} dF \quad (5.29)$$

And so an increase in the total entropy of the universe is the same thing as a *decrease* in the Helmholtz free energy of the system. So, we can forget about the reservoir and just remember that the system will do whatever it can to *minimize* its Helmholtz free energy.

If instead we let of the volume of the system change but keep it at the same constant pressure as the reservoir, then the same line of reasoning gives

$$dS_{\text{total}} = -\frac{1}{T} dG \quad (5.30)$$

so the Gibbs free energy tends to decrease too. In summary,

- At constant energy and volume, S tends to increase.
- At constant temperature and volume, F tends to decrease.
- At constant temperature and pressure, G tends to decrease.

Extensive and Intensive Quantities

One way to organise all of the thermodynamic quantities is to pick out the ones that double if you simply double the amount of stuff, adding the new alongside what you had originally. Under this hypothetical operation, you end up with twice the energy, twice the volume, but *not* twice the temperature. The quantities that *do* double are called **extensive quantities**. Those quantities that are *unchanged* when the amount of stuff doubles are called **intensive quantities**:

Extensive: V, N, S, U, H, F, G , mass

Intensive: T, P, μ , density

If you multiply an extensive quantity by an intensive quantity, you end up with an extensive quantity (e.g. volume \times density = mass). By the same token, if you divide one extensive quantity by another, you get an intensive quantity. If you multiply two extensive quantities together, you get something that is *neither*.

Adding two quantities of the same type yields another quantity of that type. Adding an extensive quantity to an intensive one isn't allowed at all. There's nothing wrong with exponentiating an extensive quantity, however you get a quantity that is **multiplicative**, e.g. $\Omega = e^{S/k}$

5 Week 5

6.2 – Average Values

In the previous week, we found the probability that a system is in any particular one of its microstates s . Suppose, though, that we're not interested in knowing all the probabilities of all the various states our system could be in but just the *average* value of some property of the system (such as its energy).

If there is a large sample of N atoms, then the average value of the energy is

$$\bar{E} = \sum_s E(s) \mathcal{P}(s) = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)} \quad (6.16 \text{ \& } 6.17)$$

where $\beta = 1/kT$. The average value of any other variable of interest can be computed in the exact same way, $\bar{X} = \sum_s X(s) \mathcal{P}(s)$.

One nice feature of average values is that they are additive; the average total energy of two objects is the sum of their individual average energies. This means that if you have a collection of many identical, independent particles, their total (average) energy is the average energy of just one, multiplied by how many there are: $U = N\bar{E}$ (6.19)

Paramagnetism

Recall that an elementary dipole in a two-state paramagnet has just two possible states: an “up” state with energy $-\mu B$, and a “down” state with energy $+\mu B$. The partition function for a single dipole is therefore

$$Z = \sum_s e^{-\beta E(s)} = e^{+\beta\mu B} + e^{-\beta\mu B} = 2 \cosh(\beta\mu B) \quad (6.20)$$

And the probabilities of finding the dipole in the “up” or “down” states are

$$\mathcal{P}_{\uparrow} = \frac{e^{+\beta\mu B}}{Z} = \frac{e^{+\beta\mu B}}{2 \cosh(\beta\mu B)} \quad \Rightarrow \quad \mathcal{P}_{\downarrow} = \frac{e^{-\beta\mu B}}{2 \cosh(\beta\mu B)} \quad (6.21 \text{ \& } 6.22)$$

The average energy of the dipole is then

$$\bar{E} = \sum_s E(s) \mathcal{P}(s) = -\mu B \left(\frac{e^{\beta\mu B} - e^{-\beta\mu B}}{2 \cosh(\beta\mu B)} \right) = -\mu B \tanh(\beta\mu B) \quad (6.23)$$

And so a collection of N of these dipoles would have energy

$$U = -N\mu B \tanh(\beta\mu B) \quad (6.24)$$

which is in agreement with equation (3.31).

Rotation of Diatomic Molecules

Rotational energies are quantized. For a diatomic molecule (like CO or HCl), the allowed rotational energies are

$$E(j) = j(j+1)\epsilon \quad (6.29)$$

where $j \in \{\mathbb{N}, 0\}$ and ϵ is a constant that is inversely proportional to the molecule's moment of inertia. The number of degenerate states for level j is $2j+1$. All of this so far assumes that the molecule is made up of two different types of atoms.

The quantity ϵ is usually only a small fraction of an electron volt, and so ϵ/k is very small. For normal to large temperatures, kT/ϵ will be much greater than 1, and so, to a good approximation, the partition function is

$$Z_{\text{rot}} \approx \int_0^\infty (2j+1)e^{-j(j+1)\epsilon/kT} dj = \frac{kT}{\epsilon} \quad (6.31)$$

In the high temperature approximation, the average rotational energy of a diatomic molecule is then

$$\bar{E}_{\text{rot}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -(\beta\epsilon) \frac{\partial}{\partial \beta} \frac{1}{\beta\epsilon} = \frac{1}{\beta} = kT \quad (\text{when } kT \gg \epsilon) \quad (6.32)$$

This is just the prediction of the equipartition theorem, since a diatomic molecule has two rotational degrees of freedom. For diatomic molecules made up of only one species of atom, turning the molecule by 180° does not change its spatial configuration, so the molecule only has *half* as many states as it otherwise would. As such (in the high temperature limit),

$$Z_{\text{rot}} \approx \frac{kT}{2\epsilon} \quad (\text{identical atoms, } kT \gg \epsilon) \quad (6.33)$$

6.3 – The Equipartition Theorem

The equipartition theorem only applies to systems with quadratic “degrees of freedom” of the form $E(q) = cq^2$ (6.34) where c is a constant coefficient and q is any coordinate or momentum variable (like x , or p_x , or L_x).

The equipartition theorem is only true in the high-temperature limit, where many distinct states contribute and therefore the spacing between the states is unimportant. In general, the equipartition theorem applies only when the spacing between energy levels is much less than kT .

6.4 – The Maxwell Speed Distribution

Technically, the probability that a molecule is moving *at* any given speed is 0 due to the continuous nature of velocity. However, the probability that some particle is moving between speeds v_1 and v_2 is given by

$$\text{Probability}(v_1 \leq v \leq v_2) = \int_{v_1}^{v_2} \mathcal{D}(v) dv \quad (6.42)$$

where \mathcal{D} is the distribution function called the **Maxwell Distribution**:

$$\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} \quad (6.50)$$

This is a way of finding the speeds of molecules in an ideal gas.

The maximum value (likelihood) of $\mathcal{D}(v)$ occurs at $v_{\text{max}} = \sqrt{2kT/m}$, and it's clear that the peak of the distribution moves to the right (increases) as the temperature increases.

The average speeds of molecules in an ideal gas is then

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad (6.52)$$

which lies between v_{max} and v_{rms} .

6.5 – Partition Functions and Free Energy

For an isolated system with fixed energy U , the most fundamental statistical quantity is the multiplicity, $\Omega(U)$ – the number of available microstates. The logarithm of the multiplicity gives the entropy, which tends to increase.

For a system in equilibrium with a reservoir at temperature T , the quantity most analogous to Ω is the partition function, $Z(T)$. Like $\Omega(U)$, the partition function is more or less equal to the number of microstates available to the system (but

at fixed temperature, not fixed energy). The entropy doesn't necessarily tend to increase in these conditions, but the Helmholtz free energy tends to *decrease* in these conditions and so

$$F = -kT \ln Z \quad \text{or} \quad Z = e^{-F/kT} \quad (6.56)$$

Using the formula above, the following useful equations can be shown

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \mu = + \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (6.64)$$

and so we can calculate all of the thermodynamic properties of a system once we know its partition function.

6.6 – Partition Functions for Composite Systems

It is useful to ask in general how the partition function for a system of several particles is related to the partition function for each individual particle. In general, for a system of N particles we have

$$Z_{\text{total}} = Z_1 Z_2 \dots Z_N \quad (\text{non-interacting, distinguishable particles}) \quad (6.69)$$

$$Z_{\text{total}} = \frac{1}{N!} Z_1^N \quad (\text{non-interacting, indistinguishable particles}) \quad (6.70)$$

where Z_1 is the partition function for any one of the particles individually. The number of ways of interchanging N particles with each other is $N!$, hence the prefactor.

6.7 – Ideal Gas Revisited

The Partition Function

As before, an ideal gas means one in which the molecules are usually far enough apart that we can neglect any energy due to forces between them. If the gas contains N molecules (all identical), then its partition function has the form of (6.70). To calculate Z_1 , we must add up the Boltzmann factors for all possible microstates of a single molecule. Each Boltzmann factor has the form

$$e^{-E(s)/kT} = e^{-E_{\text{tr}}(s)/kT} e^{-E_{\text{int}}(s)/kT} \quad (6.72)$$

where E_{tr} is the molecule's translational kinetic energy and E_{int} is its *internal energy* (rotational, vibrational, etc), for the state s . Then $Z_1 = Z_{\text{tr}} Z_{\text{int}}$

where

$$Z_{\text{tr}} = \sum_{\text{translational states}} e^{-E_{\text{tr}}(s)/kT} \quad \text{and} \quad Z_{\text{int}} = \sum_{\text{internal states}} e^{-E_{\text{int}}(s)/kT} \quad (6.74)$$

With some wavefunction in a box quantum magic, the translational partition function is described by

$$Z_{\text{tr}} = \frac{V}{v_Q} \quad (6.82)$$

where V is the total volume of the box, and v_Q is the **quantum volume** (composed of the **quantum length** cubed)

$$l_Q \equiv \frac{h}{\sqrt{2\pi m k T}} \quad \Rightarrow \quad v_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi m k T}} \right)^3 \quad (6.80 \text{ \& } 6.83)$$

Aside from the factor of π , the quantum length is the de Broglie wavelength of a particle of mass m whose kinetic energy is kT . For a box of length L , the ratio L/l_Q is quite large (for a realistic box of macroscopic size), and so the ratio V/v_Q is too.

The translational partition function is essentially the number of de Broglie-wavelength cubes that would fit inside the entire volume of the box, and is large under ordinary conditions. Combining this result with (6.73), we get

$$Z_1 = \frac{V}{v_Q} Z_{\text{int}} \quad \Rightarrow \quad Z = \frac{1}{N!} \left(\frac{V Z_{\text{int}}}{v_Q} \right)^N \quad (6.84 \text{ \& } 6.85)$$

where the logarithm of the partition function is

$$\ln Z = N (\ln V + \ln Z_{\text{int}} - \ln N - \ln v_Q + 1) \quad (6.86)$$

6 Week 6

3.5 – Diffusive Equilibrium and Chemical Potential

Consider two systems that are free to exchange both energy and particles (with fixed volumes for simplicity), and assume that both systems are made of the same species of particles. For the two systems,

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad \text{at equilibrium} \quad (3.53)$$

where the partial derivatives are taken at fixed energy and volume. The **chemical potential** is similar to this and is given by

$$\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad (3.55)$$

This is the quantity that is the same for both of the systems when they're in diffusive equilibrium:

$$\mu_A = \mu_B \quad \text{at equilibrium} \quad (3.56)$$

If the two systems are not in equilibrium, then the one with the larger value of $\partial S/\partial N$ will tend to gain particles, since it will thereby gain more entropy than the other loses. However, because of the minus sign in the definition of the chemical potential, this system has the *smaller* value of μ . Therefore, particles tend to flow from the system with higher μ into the system with lower μ .

Another useful formula for chemical potential is

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (3.60)$$

This says that μ has units of energy, specifically, μ is the amount by which a system's energy changes when you add particles and keep the entropy and volume fixed. Normally, to hold the entropy (or multiplicity) fixed, you must *remove* energy as you add a particle, so μ is negative.

If a system contains several types of particles, then each species has its own chemical potential. The generalised thermodynamic identity is then

$$dU = T dS - P dV + \sum_i \mu_i dN_i \quad (3.66)$$

If two systems are in diffusive equilibrium, the chemical potentials must be separately equal for each species (e.g. $\mu_{1A} = \mu_{1B}$, $\mu_{2A} = \mu_{2B}$, and so on).

7.1 – The Gibbs Factor

In deriving the Boltzmann factor in section 6.1, the small system and reservoir were allowed to exchange energy but not particles. It is often useful to consider a system that *can* exchange particles with its environment.

When accounting for a change in the number of particles, the probability of some state of a system is

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT} \quad (7.6)$$

Where the exponential factor is called the **Gibbs factor**:

$$\text{Gibbs factor} = e^{-[E(s) - \mu N(s)]/kT} \quad (7.5)$$

and the quantity \mathcal{Z} is called the **grand partition function** or the **Gibbs sum**. As with the partition function,

$$\mathcal{Z} = \sum_s e^{-[E(s) - \mu N(s)]/kT} \quad (7.7)$$

where the sum runs over all possible states (including all possible values of N). A hypothetical set of systems with the probabilities assigned according to equation (7.6) is called a **grand canonical ensemble**.

If more than one type of particle can be present in the system, then the μN term becomes a sum over the species. For a two species system (as an example),

$$\text{Gibbs factor} = e^{-[E(s) - \mu_A N_A(s) - \mu_B N_B(s)]/kT} \quad (\text{two species}) \quad (7.8)$$

7 Week 7

7.2 – Bosons and Fermions

The most important application of Gibbs factors is to **quantum statistics**, the study of dense systems in which two or more identical particles have a reasonable chance of wanting to occupy the same single-particle state. In this situation, the partition function for a system of N indistinguishable, non-interacting particles,

$$Z = \frac{1}{N!} Z_1^N \quad (7.16)$$

breaks down. The problem is that the counting factor of $N!$, the number of ways of interchanging the particles among their various states, is correct only if the particles are always in *different* states.

Some types of two identical particles can occupy the same state, while others can't. Particles that *can* share a state with another of the same species are called **bosons**. Bosons have integer spin (0, 1, 2, etc in units of $\hbar/2\pi$), but this is *not* the definition of a boson, just a fact of nature. Some examples of bosons are photons, pions, helium-4 atoms, etc. Many types of particles *cannot* share a state with another particle of the same type due to a quirk of quantum mechanics, and are called **fermions**. Some examples of fermions are electrons, protons, neutrons, neutrinos, helium-3 atoms, etc, and all have half-integer spin (1/2, 3/2, etc). The rule that two identical fermions cannot occupy the same state is called the **Pauli exclusion principle**.

In many situations, however, it just doesn't matter whether the particles in a fluid are bosons or fermions. When the number of available single-particle states is much greater than the number of particles, $Z_1 \gg N$ (7.17), the chance of any two particles wanting to occupy the same state is negligible. More precisely, only a tiny fraction of all system states have a significant number of states doubly occupied.

For an ideal gas, the condition (7.17) reads

$$\frac{V}{N} \gg v_Q \quad (7.19)$$

which says that the average distance between particles must be much greater than the average de Broglie wavelength (where v_Q is given by equation (6.83) further up). Notice that (7.19) depends not only on the density of the system, but on the temperature and mass of the particles through v_Q .

The Distribution Functions

When a system violates the condition $Z_1 \gg N$, we can use Gibbs factors instead. The idea is to first consider a “system” consisting of *one single-particle state*, rather than a particle itself. Thus the system will consist of a particular spatial wavefunction. The “system” and the “reservoir” occupy the same physical space.

Let's concentrate on just one single-particle state of a system, whose energy when occupied by a single particle is ϵ . When the state is unoccupied, its energy is 0; if it can be occupied by n particles, then the energy will be $n\epsilon$. The probability of the state being occupied by n particles is

$$\mathcal{P}(n) = \frac{1}{\mathcal{Z}} e^{-(n\epsilon - \mu n)/kT} = \frac{1}{\mathcal{Z}} e^{-n(\epsilon - \mu)/kT} \quad (7.20)$$

where \mathcal{Z} is the grand partition function. If the particles in question are fermions, then n can only be 0 or 1, so the grand partition function is

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} \quad (\text{fermions}) \quad (7.21)$$

From this, we can compute the probability of a state being occupied or unoccupied, as a function of ϵ , μ , and T . We can also compute the average number of particles in the state, also called the **occupancy** of the state:

$$\bar{n} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1} \quad (\text{fermions}) \quad (7.22)$$

The above is called the **Fermi-Dirac distribution**, and is referred to by \bar{n}_{FD} . The Fermi-Dirac distribution goes to zero when $\epsilon \gg \mu$, and to 1 when $\epsilon \ll \mu$. Thus, states with energy much less than μ tend to be occupied, while states with energy much greater than μ tend to be unoccupied.

If instead the particles in question are bosons, then n can be any nonnegative integer, so the grand partition function is

$$\mathcal{Z} = \frac{1}{1 - e^{-(\epsilon - \mu)/kT}} \quad (\text{bosons}) \quad (7.24)$$

In this case, μ must be less than ϵ . Meanwhile, the average number of particles in the state is given by the **Bose-Einstein distribution**

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1} \quad (\text{bosons}) \quad (7.28)$$

Like the Fermi-Dirac distribution, the Bose-Einstein distribution goes to zero when $\epsilon \gg \mu$. Unlike the FD dist., however, it goes to infinity as ϵ approaches μ from above.

To better understand the Fermi-Dirac and Bose-Einstein distributions, it's useful to ask what \bar{n} would be for particles obeying *Boltzmann* statistics. In this case, the average occupancy can be written

$$\bar{n}_{\text{Boltzmann}} = e^{-(\epsilon-\mu)/kT} \quad (7.31)$$

When ϵ is sufficiently greater than μ , so that this exponential is very small, we can neglect the 1 in the denominator of either the Fermi-Dirac distribution or the Bose-Einstein distribution, and both reduce to the Boltzmann distribution. The equality of the three distributions is in this limit, $(\epsilon - \mu)/kT \gg 1$.

A.5 – Systems of Many Particles

A system of two quantum-mechanical particles has only *one* wavefunction. In one spatial dimension, the wavefunction of the two-particle system is a function of two variables, x_1 and x_2 , corresponding to the positions of the two particles.

Some two-particle wavefunctions can be factored into a product of single-particle wavefunctions:

$$\Psi(x_1, x_2) = \Psi_a(x_1)\Psi_b(x_2) \quad (A.25)$$

This is valid only for a tiny fraction of all two-particle wavefunctions, but fortunately all *other* two-particle wavefunctions can be written as linear combinations of wavefunctions that factor in this way.

If the two particles in question are distinguishable from each other, then that's it. But, quantum mechanics also allows for particles to be absolutely *indistinguishable*. In this case, the square of the wavefunction must be unchanged under the operation of interchanging its two arguments:

$$|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2 \quad (A.26)$$

This almost implies that Ψ itself is unchanged under this operation, but not quite; another possibility is for Ψ to change sign. For bosons, Ψ is unchanged under interchange of its arguments, while Ψ changes sign for fermions:

$$\Psi(x_1, x_2) = \begin{cases} +\Psi(x_1, x_2) & \text{for bosons,} \\ -\Psi(x_1, x_2) & \text{for fermions.} \end{cases} \quad (A.28)$$

In the first case, we say that Ψ is “symmetric”, while in the second case we say that Ψ is “antisymmetric”. The wavefunction of a system of several identical bosons must be unchanged under the interchange of *any* pair of the corresponding arguments, while the wavefunction of a system of several identical fermions must change sign under the interchange of any pair. Any given single-particle state (where “state” means both the spatial wavefunction and the spin configuration) can hold arbitrarily many identical bosons, but at most one fermion.

8 Week 8

7.3 – Degenerate Fermi Gases

As a first application of quantum statistics, consider a “gas” of fermions at very low temperature. By “very low temperature”, we mean that the condition for Boltzmann statistics to apply to an ideal gas, $V/N \gg v_Q$, is badly violated so that in fact $V/N \ll v_Q$.

Zero Temperature

At $T = 0$, the Fermi-Dirac distribution becomes a step function. All single-particle states with energy less than μ are occupied, while all states with energy greater than μ are unoccupied. In this context, μ is also called the **Fermi energy**, denoted $\epsilon_F \equiv \mu(T = 0)$ (7.33). When a gas of fermions is so cold that nearly all states below ϵ_F are occupied while nearly all states above ϵ_F are unoccupied, it is said to be *degenerate*.

The value of ϵ_F is determined by the total number of electrons present. In order to calculate ϵ_F , make the approximation that the electrons are *free* particles, subject to no forces except that they are confined within a box of volume $V = L^3$. The definite-energy wavefunctions of a free electron inside a box are just sine waves. For a three-dimensional box, the momentum vectors are

$$p_x = \frac{hn_x}{2L} \quad p_y = \frac{hn_y}{2L} \quad p_z = \frac{hn_z}{2L} \quad (7.35)$$

where (n_x, n_y, n_z) is a triplet of positive integers. The allowed energies are therefore

$$\epsilon = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \quad (7.36)$$

To visualise the set of allowed states, it's helpful to draw a picture of “ n -space”, the three-dimensional space whose axes are n_x , n_y , and n_z . Each allowed \vec{n} vector corresponds to a point in this space with positive integer coordinates; the set of all allowed states forms a huge lattice filling the first octant of n -space. Each lattice point actually represents *two* states, since for each spatial wavefunction there are two independent spin orientations.

In n -space, the energy of any state is proportional to the square of the *distance* from the origin, $n_x^2 + n_y^2 + n_z^2$. So, as we add electrons to the box, they settle into states starting at the origin and gradually working outward. By the time all of the electrons are added, the total number of occupied states is so huge that the occupied region of n -space is essentially an eighth of a sphere, with radius n_{\max} .

Now, the Fermi energy $\mu = \epsilon_F$ is the energy of a state that sits just on the surface of the sphere in n -space, so

$$\epsilon_F = \frac{h^2 n_{\max}^2}{8mL^2} \quad (7.37)$$

The total volume of the eighth-sphere in n -space equals the number of lattice points enclosed, and so the total number of occupied states is twice the volume of the eighth-sphere (due to the two spin orientations): $N = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{\max}^3 = \frac{\pi}{3} n_{\max}^3$ (7.38). Combining the above two equations gives the Fermi energy as a function of N and the total volume of the box:

$$\epsilon_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \quad (7.39)$$

Although this was derived for a cubic box, it applies for electrons in any macroscopic container of any shape.

Using spherical coordinates (where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$), the total energy of all electrons is

$$U = 2 \int_0^{n_{\max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin \theta \epsilon(n) = \pi \int_0^{n_{\max}} \epsilon(n) n^2 dn = \frac{\pi h^2}{8mL^2} \int_0^{n_{\max}} n^4 dn = \frac{\pi h^2 n_{\max}^5}{40mL^2} = \frac{3}{5} N \epsilon_F \quad (7.41 \text{ \& } 7.42)$$

The *average* energy of the electrons is therefore $3/5$ the Fermi energy.

Comparing the Fermi energy to the average thermal energy is essentially the same as comparing the quantum volume to the average volume per particle,

$$\frac{V}{N} \ll v_Q \quad \text{is the same as} \quad kT \ll \epsilon_F \quad (7.43)$$

When this condition is met, the approximation $T \approx 0$ is fairly accurate for many purposes, and the gas is said to be degenerate. The temperature that a Fermi gas would have to have in order for kT to equal ϵ_F is called the **Fermi temperature**: $T_f \equiv \epsilon_F/k$.

Using the formula $P = -(\partial U / \partial V)_{S,N}$, we can calculate the pressure of a degenerate electron gas:

$$P = -\frac{\partial}{\partial V} \left[\frac{3}{5} N \frac{h^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3} V^{-2/3} \right] = \frac{2N\epsilon_F}{5V} = \frac{2}{3} \frac{U}{V} \quad (7.44)$$

which is called the **degeneracy pressure**. Degeneracy pressure is what keeps matter from collapsing under the huge electrostatic forces that try to pull electrons and protons together.

A more measurable quantity is the **bulk modulus**, that is, the change in pressure when the material is compressed, divided by the fractional change in volume:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{10}{9} \frac{U}{V} \quad (7.45)$$

Small Nonzero Temperatures

The total energy of a degenerate Fermi gas for $T \ll \epsilon_F/k$ is

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F} \quad (7.47)$$

Where the heat capacity can be easily computed from this as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\pi^2 N k^2 T}{2\epsilon_F} \quad (7.48)$$

The heat capacity goes to zero at $T = 0$ as required by the third law of thermodynamics. The approach to zero is *linear* in T .

The Density of States

The number of single-particle states per unit energy is called the ***density of states***. The symbol for it is $g(\epsilon)$, and it can be written in various ways:

$$g(\epsilon) = \frac{\pi(8m)^{3/2}}{2h^3}V\sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}}\sqrt{\epsilon} \quad (7.51)$$

If you want to know how many states there are between two energies ϵ_1 and ϵ_2 , you just integrate this function over the desired range. The density of states is a function whose purpose is to be integrated. Equation (7.51) is for the specific case of a gas of “free” electrons, confined inside a fixed volume but not subject to any other forces.

For an electron gas at *zero* temperature, we can get the total number of electrons by just integrating the density of states up to the Fermi Energy:

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (T = 0) \quad (7.52)$$

But what if $T \neq 0$? Then we need to multiply $g(\epsilon)$ by the *probability* of a state with that energy being occupied, that is, the Fermi-Dirac distribution function. Also, we need to integrate up to infinity, since any state could conceivably be occupied:

$$N = \int_0^\infty g(\epsilon)\bar{n}_{\text{FD}}(\epsilon) d\epsilon = \int_0^\infty g(\epsilon)\frac{1}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon \quad (\text{any } T) \quad (7.53)$$

And to get the total energy of all the electrons, just slip in an ϵ :

$$U = \int_0^\infty \epsilon g(\epsilon)\bar{n}_{\text{FD}}(\epsilon) d\epsilon = \int_0^\infty \epsilon g(\epsilon)\frac{1}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon \quad (\text{any } T) \quad (7.54)$$

The chemical potential μ is the point where the probability of a state being occupied is exactly 1/2, and it's important to note that this point is no longer the same as it was at zero temperature: $\mu(T) \neq \epsilon_F$ except when $T = 0$ (7.55).

9 Week 9

The Sommerfeld Expansion

The method for finding the chemical potential and total energy of a free electron gas in the limit $kT \ll \epsilon_F$ is called the Sommerfeld expansion.

After a lot of approximating and integration, we obtain that $\mu/\epsilon_F \sim 1$, with

$$\frac{\mu}{\epsilon_F} = 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \quad (7.66)$$

The chemical potential gradually decreases as T is raised.

The integral (7.54) for the total energy can be evaluated as well, resulting in

$$U = \frac{3}{5}N\frac{\mu^{5/2}}{\epsilon_F^{3/2}} + \frac{3\pi^2}{8}N\frac{(kT)^2}{\epsilon_F} + \dots = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F} + \dots \quad (7.67 \text{ \& } 7.68)$$

7.6 – Bose-Einstein Condensation

A gas of bosons will abruptly “condense” into the ground state as the temperature goes below a certain critical value. It’s simplest to first consider the limit $T \rightarrow 0$. At zero temperature, all the atoms will be in the lowest-energy available state, and since arbitrarily many bosons are allowed in any given state, this means that every atom will be in the ground state. For atoms confined to a box of volume $V = L^3$, the energy of the ground state is

$$\epsilon_0 = \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = \frac{3h^2}{8mL^2} \quad (7.118)$$

At any temperature, the average number of atoms in this state N_0 , is given by the Bose-Einstein distribution:

$$N_0 = \frac{1}{e^{(\epsilon_0 - \mu)/kT} - 1} \quad (7.119)$$

when T is sufficiently low, N_0 will be large. How low must the temperature be in order for N_0 to be large?

We have the condition that the sum of the Bose-Einstein distribution over *all* states must add up to the total number of atoms, N . When $kT \gg \epsilon_0$, we can approximate the sum as an integral with

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon \quad (7.122)$$

where the function $g(\epsilon)$ is the density of states: the number of single-particle states per unit energy. For spin-zero bosons confined in a box of volume V , this function is the same as in equation (7.51), but divided by 2 because now there is only one spin orientation:

$$g(\epsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \sqrt{\epsilon} \quad (7.123)$$

Eventually we get that

$$N = 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad (7.125)$$

which is only correct for one particular temperature, T_c :

$$N = 2.612 \left(\frac{2\pi mkT_c}{h^2} \right)^{3/2} V \quad \text{or} \quad kT_c = 0.527 \left(\frac{h^2}{2\pi m} \right) \left(\frac{N}{V} \right)^{2/3} \quad (7.126)$$

At temperatures higher than T_c , the chemical potential is negative and essentially all of the atoms are in excited states. At temperatures lower than T_c , the chemical potential is very close to zero and the number of atoms in excited states is given by

$$N_{\text{excited}} = \left(\frac{T}{T_c} \right)^{3/2} N \quad (T < T_c) \quad (7.128)$$

The rest of the atoms must be in the ground state, so

$$N_0 = N - N_{\text{excited}} = \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right] N \quad (T < T_c) \quad (7.129)$$

The abrupt accumulation of atoms in the ground state at temperatures below T_c is called ***Bose-Einstein condensation***. The transition temperature T_c is called the ***condensation temperature***, while the ground-state atoms themselves are called the ***condensate***.

The condensation temperature is (aside from a factor of 2.612) precisely the temperature at which the quantum volume ($v_Q = (h^2/2\pi mkT)^{3/2}$) equals the average volume per particle (V/N). In other words, if we imagine the atoms being in wavefunctions that are as localized in space as possible, then condensation begins to occur just as the wavefunctions begin to overlap significantly.

10 Week 10

11 Week 11

12 Week 12

13 Week 13