

Statistical mechanics

January 11, 2017

1 Introduction and the first law

The subjects of statistical mechanics and thermodynamics are large everyday objects, containing billions of individual constituents. Examples include say 1 liter of a certain gas or liquid, or electrons in a metallic wire, or lattice vibrations of a crystal, or photons coming from an incandescent light bulb. For such objects, you cannot possibly follow the motion of individual particles, nor would you be interested to do so, even if you could. So instead you presume that the particles are moving somewhat at random, and use the laws of probability to figure out the average properties of the assembly of particles.

The description of the properties of microscopic bodies based on the statistical properties of the constituent particles is known as statistical physics. It is interesting that statistical physics represents a relatively late approach to the subject, the one which was first practiced in earnest in the late 19th century. The development of this subject is associated with Maxwell, Boltzmann, and Gibbs. A great deal was discovered about the thermal properties of microscopic bodies in the early 19th century, when even the existence of atoms was not universally accepted. The development of this so called thermodynamics is associated with many names, including Carnot (Carnot cycle), Joule (Joule heating, unit of energy), and Clausius (entropy).

Due to its dual nature, the subject is notoriously difficult to teach. In teaching my graduate Stat Mech class I am borrowing material from more than 10 books. In this class, I will rely primarily on Schroeder's text. The standard old text is Reif, which is great, but it is definitely too long for 1 semester. I recommend you to familiarize yourself with this text. More books are listed on my webpage.

1.1 Temperature

Let us start by slowly introducing the temperature, which is the quantity that is equal between two bodies in a thermal equilibrium. What is the thermal equilibrium? It is the

situation which is reached after two or more bodies are brought into a thermal contact, where they can exchange heat, and enough time has passed to let the combined system relax. There are many important caveats about this definition. First, I will rely on you knowing that heat is the energy of the internal motion of atoms and molecules inside a body. Second, one has to assume this thermal equilibrium is eventually reached. Third, we will later see that more than two bodies can be in a thermal equilibrium, a fact familiar from our everyday experience, but not obvious a priori.

When two objects are approaching the thermal equilibrium, the one which gives away energy is said to be at a higher temperature, while the one that accepts energy is at lower temperatures. At this point, we cannot define the temperature any better than that, but eventually we will be able to calculate the temperature for a given microscopic model of the object. To make some progress till then, we will rely on this loose definition of temperature.

1.2 Ideal gas

One can make a variety of practical thermometers based on the change of volume, resistance, color etc. of various substances. Particularly interesting is a thermometer based on the ideal gas. The ideal gas is an abstraction, a model of a gas made of non-interacting particles. Many real gases behave as an ideal gas at high T and low density. The pressure of such dilute gases increases with temperature, and may serve as a thermometer. One can experimentally observe that for thermometers made of different amounts of different gases the P vs. T curves are proportional to each other, allowing for a uniform definition of T in this way. Furthermore, as temperature is lowered, the pressure extrapolates to zero, indicating the existence of the lowest temperature, the absolute zero. The Kelvin temperature scale (named after William Thompson) measures temperature from that point and assumes that the temperature of the ideal gas proportional to its pressure. The units, or degrees, of this scale are taken equal to degrees Celsius.

Specifically, it was found that $PV = NkT$, where V is the volume of the gas, N is the number of particles (atoms or molecules) and k (or k_B) is Boltzmann's constant, $1.38 \cdot 10^{-23}$ J/K. The 10^{-23} factor should not be surprising, because the number of molecules in a typical amount of gas that we encounter is equally big. In fact, we commonly use the Avogadro number $N_A = 6.022 \times 10^{23}$ to measure the number of atoms or molecules. N_A molecules of a certain chemical is known as a mole. Why this number and not 10^{23} or 10^{24} ? Because this way one mole of protons or neutrons weighs about one gram. More precisely, one mole of ^{12}C weighs about 12 grams. If the number of moles is n , the number of molecules is $N = nN_A$, so that $PV = nN_AkT \equiv nRT$.

Problem 1.11 Rooms A and B are the same size. A is warmer than B. Which one contains more air molecules?

Problem 1.12 Calculate the average distance between molecules in air. Compare to the size of the molecules.

The volume per molecule is $V/N = kT/P = 1.4 \cdot 10^{-23} \text{J/K} \cdot 300\text{K}/10^5 \text{Pa} \approx 4 \cdot 10^{-26} \text{m}^3$. The distance is cubic root of that, $\approx 3.5 \text{ nm}$, which is 10-100 times larger than the size of the molecules. (Bohr radius is 0.05 nm. Molecular bonds are a few Angstrom.) This is partially the reason why we can think of the common gases at room T as ideal.

1.3 Microscopic model

Let us now discuss the microscopic properties of the ideal gas in order to see why $P \propto N/V$, and what is this quantity T in the RHS physically represents. (Hint: we defined T through the energy exchange. For the ideal gas, T will directly represents the energy. But this is not generally true.)

Simplistic model of a ball elastically bouncing in a cylindrical (square!) container. $\bar{P} = \bar{F}/A = \frac{\Delta p_x}{\Delta t}/A$. At each collision, the particle velocity is reversed, $\Delta p_x = 2mv_x$; the time between collisions with the piston $\Delta t = 2L/v_x$, so that $\bar{P} = \frac{mv_x^2}{LA}$. LA is of course the volume. For N particles, we have N similar contributions. Averaging over the number of particles $\langle \rangle$, the time-and-particle averaged pressure is $\langle \bar{P} \rangle = \frac{m\langle v_x^2 \rangle}{V}$. We can of course drop averaging in $\langle \bar{P} \rangle$ – the measured pressure is the average result from multiple particles colliding with the piston over time.

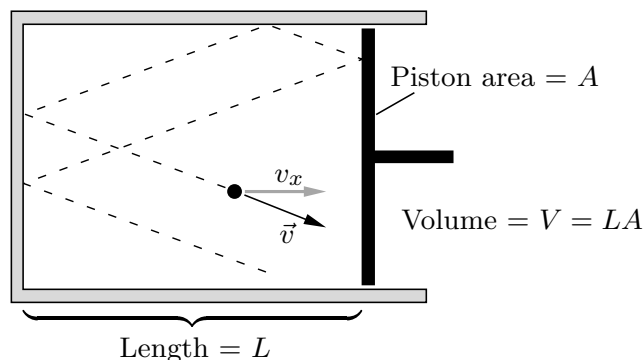


Figure 1.4. A greatly simplified model of an ideal gas, with just one molecule bouncing around elastically. Copyright ©2000, Addison-Wesley.

Assuming the system is isotropic (all directions are equivalent), $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. Also, $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v^2 \rangle$, so that $\langle v_x^2 \rangle = \langle v^2 \rangle/3$. Therefore, $PV = m\langle v^2 \rangle/3 = \frac{2}{3}N\langle K \rangle$. Going back to our ideal gas law, $PV = NkT$, we see that $\langle K \rangle = \frac{3}{2}kT$. This relation explains the special importance of the ideal gas in measuring the temperature – in this case, the temperature is directly proportional to the mean kinetic energy of the particles.

At this point, we may want to estimate the scale of this energy. Let us measure the energy in eV, $1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$. kT at room temperature (300 K) is then $1.38 \cdot 10^{-23} \cdot 300 / 1.6 \cdot 10^{-19} \text{ eV} \approx 25 \text{ meV}$. We see that this energy is too small to knock electrons out of atoms (good!), but could high enough to cause excitations (vibrations and rotations) in multi-atomic molecules.

1.4 Equipartition theorem

In addition to the kinetic energy, many forms of energy are quadratic in position or velocity. E.g. $L^2/2I$ (rotation), $kx^2/2$ (vibrations). Each such term is referred to as a degree of freedom. (Beware that the notation may be somewhat different in other disciplines. Normally, degrees of freedom is the number of independently variable parameters.) It turns out that each quadratic degree of freedom contributes on average $kT/2$ to the total energy: thermal $U = NfkT/2$, where f is the number of degrees of freedom.

Example: diatomic molecule. 3 translations, 2 rotations perpendicular to the axis, 1 vibration.

This is a classical result. In quantum mechanics, we know that the energies are quantized, so kT may be much smaller than the energy spacing. (We will estimate the rotational and vibrational energies later, in Ch. 6.) In this case, some of the degrees of freedom may be not activated. A degree of freedom will be activated when the kinetic energy of the particles (recall $\langle K \rangle = \frac{3}{2}kT$) becomes comparable or larger than to the corresponding energy spacing. Therefore, we expect that U to be made of roughly straight segments $NfkT/2$ with f growing with T as more degrees of freedom are activated. There are also some additive constants terms (binding energy of electrons, rest energy of all particles) that are not actively involved and we cannot easily observe when changing T . Therefore, it makes sense to talk about $\partial U / \partial T$, which is called the heat capacity, C . According to the equipartition theorem, $C = Nfk/2$.

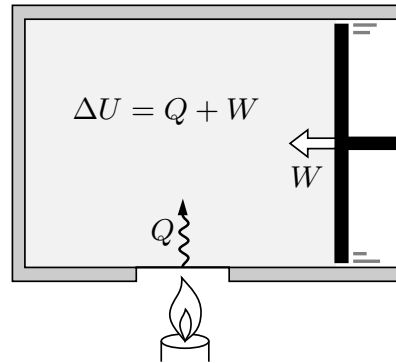
Example: In a solid, the number of degrees of freedom is 6 (3 coordinates and 3 velocities, or $3 kx^2/2$ and $3 mv^2/2$). Therefore the expected heat capacity is $C = 3Nk$ (the rule of Delong and Petit). This is grossly violated at low temperatures, which puzzled physicists 100 years ago, and caused Einstein model (naive) and later Debay model (captures essential physics).

1.5 Heat and Work

Forms of energy. Energy exchange between 2 bodies or a body and a surrounding. Distinguish 2 cases: 1) external parameters change, so that energy levels of the body change

(work) or 2) external parameters do not change, so that the energy levels of the body do not change (thermal interactions). Heat is the “mean energy transfer between 2 systems as a result of a purely thermal interaction.” Total U is conserved, but the forms can change. Heat: spontaneous flow of energy between bodies. Figure 1.7. Work: any other transfer of energy, e.g. pushing a piston, stirring, applying fields. The first law of thermodynamics: $\Delta U = Q + W$ – energy conservation. Writing ΔQ and ΔW is discouraged, because these are not potential energies, and the result depends on the details of the trajectory, not only the initial and the final points.

Figure 1.7. The total change in the energy of a system is the sum of the heat added to it and the work done on it. Copyright ©2000, Addison-Wesley.



The mechanical work is the most intuitive, so we will mostly deal with it. However, many types of work can be considered, e.g. magnetic one, and the formalism can be reproduced. Compression work: $W = F\Delta x$ (Δx is positive when directed inward: the world works on the system.) Or, $W = PA\Delta x = -P\Delta V$ (ΔV is positive when volume grows). Sign: work done by the external entity is positive when the gas is forced to contract, $\delta V < 0$.

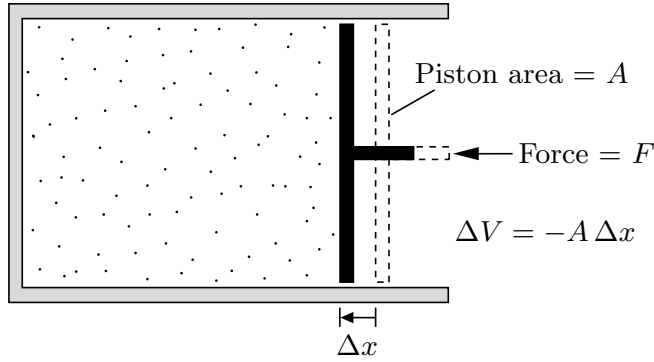
Important: for the pressure to be well-defined, the volume should be changed slow enough. Such a process is referred to as **quasistatic**. The word (‘static’) should not confuse you – there are even stricter demands for slowness of other processes. Here, the process should be slower than the pressure equilibrates in the container, which is determined by the speed of sound – quite fast.

Now suppose $\delta V/V$ is not small, so that P will be changing even if the process is quasistatic. Then $W = -\int PdV$. Example: square cycle, engine.

1.6 Heat and Work in the ideal gas

There are two special ways (and actually, many other ways in between) to compress an ideal gas. One can let it thermalize at each point along the way – “**isothermal**” compression. For that heat has to flow between the gas and the container, so the process has to be slow. Or one can do it fast enough, so that the heat does not have time to flow –

Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$. Copyright ©2000, Addison-Wesley.



“**adiabatic**” compression. Note that in quantum-mechanical context, ‘adiabatic’ means ‘slow’. (The relation between the two uses of the word will become clear when we discuss statistics.)

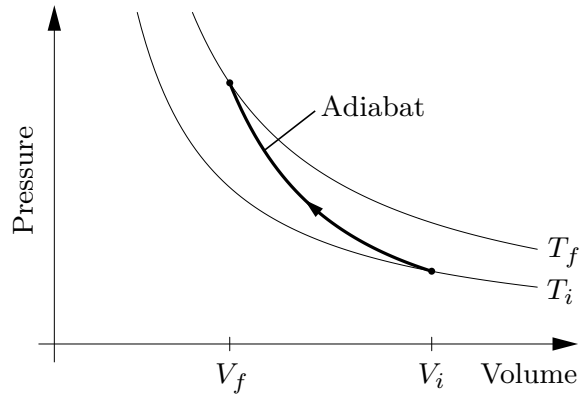
Isotherm. $W = - \int_{V_i}^{V_f} P dV = -NkT \int_{V_i}^{V_f} \frac{1}{V} dV = NkT \ln \frac{V_i}{V_f}$. Sign: if the gas is compressed, $V_i > V_f$ and $W > 0$. As the gas is compressed, the energy must flow out of it in the form of heat. Indeed, $Q = \Delta U - W = \Delta(NfkT/2) - W = 0 - W = NkT \ln \frac{V_f}{V_i}$. (Here, we used the fact that according to equipartition theorem, $U = NfkT/2$, the energy of the *ideal* gas is constant for constant T.) Sign: if the gas is expanding, $V_f > V_i$, so that $Q > 0$ – one needs to provide heat to keep the expanding gas isothermal while working on the piston.

Adiabat: Let us not allow any heat exchange $Q = 0$, $\Delta U = W$. When W is positive (compression) $\Delta U > 0$, so that according to $U = NfkT/2$ the temperature should increase. I.e. adiabat is more steep on the $P - V$ plane. Infinitesimal change of it is $dU = NfkdT/2$. Infinitesimal work is $-PdV$, and $\Delta U = W$ means $NfkdT/2 = -PdV$. We got a differential equation for relating T and V in the adiabatic process. Expressing P through the ideal gas law, $\frac{f}{2} \frac{dT}{T} = -\frac{dV}{V}$, $\frac{f}{2} \ln \frac{T_f}{T_i} = -\ln \frac{V_f}{V_i}$, $V_f T_f^{f/2} = V_i T_i^{f/2}$, or $VT^{f/2} = const$. Alternatively, re-expressing T through P , we get $V^\gamma P = const$, where γ is the adiabatic exponent, $(f + 2)/2$. Since $\gamma > 1$, adiabat is indeed steeper than isotherm.

1.7 Heat capacity – revisited

In fact, our definition of heat capacity was incomplete. The correct definition is $C \equiv Q/\Delta T$. If $V = const$, no work is done and $\Delta U = Q$ as we assumed earlier. Then indeed, $C_V = (\partial U/\partial T)_V$. But if the volume is changing, $C = \frac{\Delta U - W}{\Delta T}$. Particularly interesting is the case of constant pressure $C_P = \frac{\Delta U - (-P\Delta V)}{\Delta T} = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$. So in

Figure 1.12. The PV curve for adiabatic compression (called an **adiabat**) begins on a lower-temperature isotherm and ends on a higher-temperature isotherm. Copyright ©2000, Addison-Wesley.



addition to the change of the internal energy (the first term), the provided head has to also provide for the work that the expanding gas performs on the outside world (the second term).

Note that this is a general formula, in which the first term $(\partial U/\partial T)_P$ is not the same as $C_V = (\partial U/\partial T)_V$. However, for the ideal gas the two are equal, because U depends only on T , and not on V or P . The second term, $P \left(\frac{\partial V}{\partial T}\right)_P = P \left(\frac{\partial(NkT/P)}{\partial T}\right)_P = Nk$. Therefore, $C_P = C_V + Nk$ (for the ideal gas only!). Incidentally, $C_P/C_V = \gamma$.

To ease the process of keeping track of the work by the gas at constant pressure as its internal energy is changing, one introduces Enthalpy, $H = U + PV$. Meaning: the total energy one needs to create the system from scratch and put it into the environment. At constant pressure, $\Delta H = \Delta U + P\Delta V$. Now, recall that $\Delta U = Q - P\Delta V$, so that $\Delta H = Q$ (at constant P , and if there are no other types of work). Hence if the temperature is changing, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$. Of course, enthalpy can change not only with T . Most relevant examples are phase transitions and chemical reactions, which happen at a constant pressure.

2 Entropy and the second law

We still have not properly defined T , and have not answered why energy flows from one body to the other as thermal equilibrium is established. It is easier to answer this second question first.

Definition: Macrostate is the state of the system characterized by microscopic observables, such as P, V, T, U . Microstate is the state of the system characterized by positions and velocities of all particles, or in the quantum case, by the knowledge of their wavefunctions. There are many microstate that to us would appear the same, that is they correspond to the same macrostate. The (huge!) number of microstates for a given macrostate is

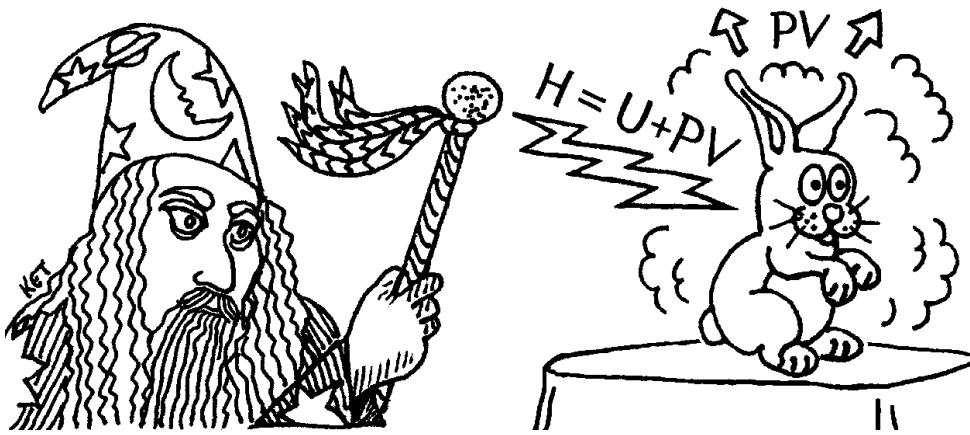


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV , to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$. Drawing by Karen Thurber. Copyright ©2000, Addison-Wesley.

called the multiplicity.

2.1 Paramagnet

Consider a naive model of a paramagnet: an assembly of N non-interacting spins $1/2$. Spin $1/2$ can have two possible projections, up and down. The system has 2^N different microstates. But I may not necessarily care which specific spins are up and which are down and may want to characterize the system only by the total magnetization of the system, $\propto M \equiv (N_{\uparrow} - N_{\downarrow})$. There are only N values M can take: $N, N-2, \dots, -N$ – one says that there are $N + 1$ macrostates. 2^N and $N + 1$ are very different numbers indeed. This means that there should be very many different microstates that correspond to some of the macrostates. The number of microstates that correspond to a macrostate is called a multiplicity, Ω . What is the multiplicity of a state with a given N_{\uparrow} ? We can choose the first spin up out of N spins in N ways, the next one in $N - 1$ ways etc., resulting in $N(N - 1)(N - 2) \dots (N - N_{\uparrow} + 1) = \frac{N!}{(N - N_{\uparrow})!}$. This procedure overcounts the number of ways to pick our microstate, because we counted separately the different orders in which the same way set of spins can be selected; we need to divide it by the number of permutations of N_{\uparrow} spins, resulting in $\Omega(N_{\uparrow}) = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} \equiv \binom{N}{N_{\uparrow}}$. (Incidentally, the expression is equal to $\frac{N!}{N_{\uparrow}!N_{\downarrow}!}$, so it is symmetric with respect to spin ups and spin downs.) $\binom{N}{N_{\uparrow}}$ is of course the binomial coefficient, and you can repeat the argument above to see that it applies to the coefficients in expansion of $(a + b)^N$ in powers of a and b .

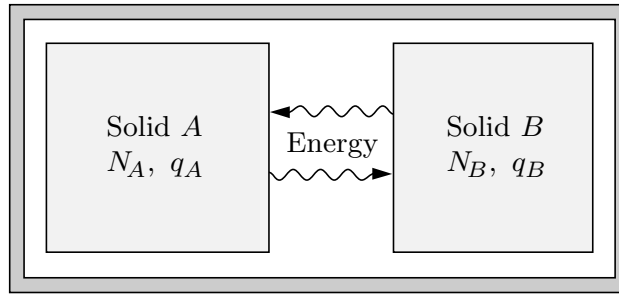


Figure 2.3. Two Einstein solids that can exchange energy with each other, isolated from the rest of the universe. Copyright ©2000, Addison-Wesley.

It may be natural to assume that all microstates of the system are equally probable. The probability to find the system in one of the macrostates is then equal to its multiplicity over the total number of microstates: $P(N_{\uparrow}) = \Omega(N_{\uparrow})/\Omega_{total}$. One can easily check that indeed, $\sum P(N_{\uparrow}) = \binom{N}{N_{\uparrow}}/2^N = 1$ by using the binomial expansion for $(1 + 1)^N$.

2.2 Einstein solid

Let us repeat this exercise for the Einstein solid, made of N oscillators each having the frequency ω . If a macrostate is only defined by the total energy of the system $U = q\hbar\omega$, then $\Omega(q, N) = \frac{(q+N-1)!}{q!(N-1)!}$ (number of ways to choose $(N-1)$ partitions out of $(q+N-1)$ partitions and energy quanta). Again, we encounter the binomial coefficient, $\binom{q+N-1}{N-1}$. In this example, the number of macrostates is not bounded from above.

Let us now consider two such solids, A and B , made from oscillators with the same frequency ω and sharing the total energy $U = q\hbar\omega$. Let them slowly exchange energy, so that the system can be in any microstate such that $q_A + q_B = q$. Let us assume now that such microstates are equally probable. Their total multiplicity is $\Omega(q, N)$ (q energy quanta shared by $N = N_A + N_B$ oscillators). We can also calculate the multiplicity of the microstates with a given value of q_A and q_B – it is simply $\Omega(q_A, N_A)\Omega(q_B, N_B)$, e.g. for any microstate of body A with q_A energy quanta, body B can be in any of its microstates with q_B energy quanta.

Again, let us make the crucial assumption that all microstates that satisfy energy conservation $q_A + q_B = q$ are equally probable. The probability of a macrostate with q_A and q_B is then $\Omega(q_A, N_A)\Omega(q_B, N_B)/\Omega(q, N)$. The statement that I want to prove next is that for reasonably large systems and energies, the distribution is extremely sharply peaked at some value of q_A and q_B . We can say that the energy exchange establishes the most probable macrostate state of the combined system – the one that has the most microstates $\Omega(q_A, N_A)\Omega(q_B, N_B)$. In yet other words, the number of ways energy can be divided be-

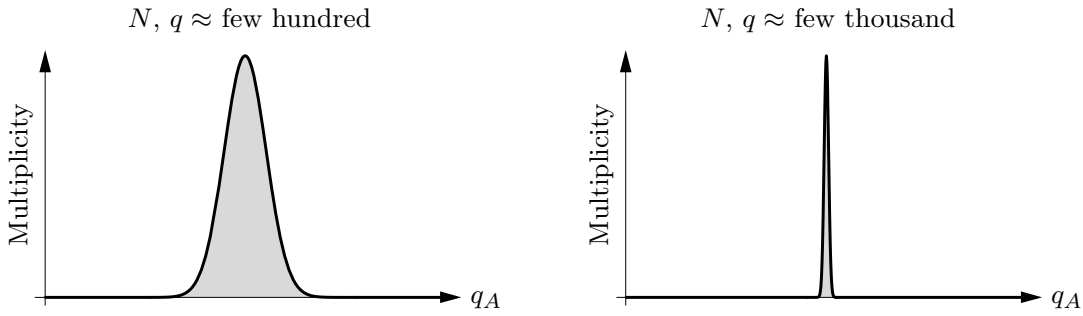


Figure 2.6. Typical multiplicity graphs for two interacting Einstein solids, containing a few hundred oscillators and energy units (left) and a few thousand (right). As the size of the system increases, the peak becomes very narrow relative to the full horizontal scale. For $N \approx q \approx 10^{20}$, the peak is much too sharp to draw. Copyright ©2000, Addison-Wesley.

tween the degrees of freedom in a microscopic body is so huge that the “most probable” state is the only one can realistically observe.

2.3 Thermal equilibrium and fluctuations

Since the numbers are very large, we can work with logarithms. We can estimate $\ln(N!)$ as $\sum_{n=0}^N \ln n \approx \int_{n=0}^N \ln x dx = N \ln N - N$. [The correction is $O(\ln N)$. In the following, we neglect terms of the order of $\ln q$ and $\ln N$.] Then

$$\ln \Omega(q, N) = \ln \left[\frac{N!}{q!} \binom{q+N}{N} \right] \approx (q+N) \ln(q+N) - (q+N) - q \ln q + q - N \ln N + N = (q+N) \ln(q+N) - q \ln q - N \ln N.$$

Let us assume $q \gg N$. This condition means that there are many quanta of energy per oscillator so the system should be classical (as opposed to quantum) and we would be able to apply the equipartition theorem late. We can now expand

$$(q+N) \ln(q+N) = (q+N) [\ln q + \ln(1 + N/q)] \approx (q+N) (\ln q + N/q + \dots) \approx (q+N) \ln q + N + \dots,$$

$$\text{and } \ln \Omega(q, N) \approx N \ln(q/N) + N + \dots = N \ln(eq/N) + \dots$$

$$\text{For 2 solids, } \ln[\Omega(q_A, N_A)\Omega(q_B, N_B)] \approx N_A \ln(q_A/N_A) + N_B \ln(q_B/N_B) + N_A + N_B + \dots = N_A \ln(q_A/N_A) + N_B \ln(q_B/N_B) + N + \dots$$

So the log of number of the microstates (which is \propto probability) depends on q_A as: $S \approx N_A \ln q_A + N_B \ln q_B + \text{const} = N_A \ln q_A + N_B \ln(q - q_A) + \text{const}$. This expression is maximal when its derivative with respect to q_A is equal to zero: $N_A/q_A - N_B/(q - q_A) = 0$, or $N_A/q_A = N_B/q_B$, or $q_{A,B} = qN_{A,B}/(N_A + N_B)$. This makes a lot of sense, as equipartition theorem tells us that $U = NkT$, so $q = NkT/\hbar\omega$, so that in thermal

equilibrium, when $T_A = T_B$, q/N should be equal to $kT/\hbar\omega$ on each side.

But we can go further than that and evaluate the effect of small deviations from the thermal equilibrium. Let δq be the deviation of $q_{A,B}$ from the most probable value: $q_A = qN_A/N + \delta q$ and $q_B = qN_B/N - \delta q$. Then $S = N_A \ln[e(qN_A/N + \delta q)/N_A] + N_B \ln[e(qN_B/N - \delta q)/N_B]$. Expanding in $\delta q/q$, we have

$$S \approx N \ln(eq/N) + N_A \delta q N / q N_A - N_B \delta q N / q N_B - N_A [\delta q N / q N_A]^2 / 2 - N_B [\delta q N / q N_B]^2 / 2$$

$$\approx N \ln(eq/N) - N^2 (1/N_A + 1/N_B) (\delta q/q)^2 / 2.$$

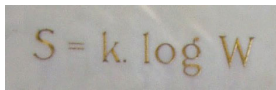
For two solids of the same size, $S \approx N \ln(eq/N) - 2N(\delta q/q)^2$. (My $N = 2N_{book}$.) Therefore, the probability to find the system in a state different from the equilibrium is $\propto \Omega(q_A, N_A)\Omega(q_B, N_B) \propto \exp[-2N(\delta q/q)^2] = \exp[-2N(\delta U/U)^2]$. Notice the squared $\delta U/U$ and linear N – these features are generic. This bell-shaped function falls very fast, with the typical width of $\delta U \sim U/\sqrt{N}$. These variations of energy (or other quantities) around the most probable value are called fluctuations.

Second law: closed macroscopic system spontaneously tend to macrostates with maximal multiplicity.

2.4 Entropy

Notice that we found it more convenient to work with $\ln \Omega$ rather than the multiplicity itself. The reason is that $\ln \Omega(q, N) \approx N \ln(eq/N) = N \ln(const U/N)$ is an extensive quantity: if we double the system size ($N \rightarrow 2N, U \rightarrow 2U$), it doubles. (Other examples of the extensive quantity are V and M . On the other hand, the intensive quantities, such as P and T do not scale with the system size.) Multiplicity on the other hand is not an extensive quantity – the multiplicity factorizes when two sub-systems are combined together. (This is the reason why $\ln \Omega$ is additive.)

We now have an extensive quantity which describes some important property of the system. We want to give it a special name $S \equiv k \ln \Omega$. This quantity is called the entropy.



$$S = k \log W$$

Based on the example of the Einstein solids, we have seen that the total entropy of the system grows when two sub-systems are put in thermal contact. This simply is the result of the system assuming a macrostate with the maximal multiplicity, purely based on the probability. This is a probabilistic statement, grounded in experimental evidence, and known as the second law of thermodynamics.

Entropy is a household name now, but it had no microscopic explanation before the works of Boltzmann and Gibbs. It was introduced in the purely thermodynamics context by Clausius in 1850-1860's based on the ideas of Carnot. One can construct the theory of thermodynamics without reference to statistics, postulating the existence of an extensive thermodynamic function (a function of N , V and U) which is maximal in equilibrium (in analogy with the potential energy of a mechanical system which is minimal in equilibrium); see Callen's book.

2.5 Detour: Stirling's approximation

Notice that $N! = \int_0^{\infty} e^{-x} x^N dx$ (by parts). Integrand: x^N rapidly grows, but e^{-x} eventually falls even faster. There will be a maximum at $-e^{-x} x^N + N e^{-x} x^{N-1} = 0$, i.e. at $x = N$. Take $x = N + y$ and expand the log of the integrand around that point: $N \ln x - x = N \ln(N) + N \ln(1 + y/N) - N - y \approx N \ln(N) + N[y/N - (y/N)^2] - N - y = N \ln(N) - N - y^2/2N$. Therefore, $N! \approx (\frac{N}{e})^N \int_{-N}^{\infty} e^{-y^2/2N} dy \approx \sqrt{2\pi N} (\frac{N}{e})^N$.

The generalization of this formula for non-integer N is the Gamma function:

$$\Gamma(\nu + 1) = \int_0^{\infty} e^{-x} x^{\nu} dx.$$

Let us use this more precise approximation to improve our evaluation of $\Omega(q, N)$: $\ln \Omega(q, N) = \ln[\frac{N}{q+N} (\frac{q+N}{N})] \approx N \ln(eq/N) + 1/2 \ln(\frac{2\pi(q+N)}{2\pi q \cdot 2\pi N}) - \ln(\frac{N}{q+N}) \approx N \ln(eq/N) + 1/2 \ln(\frac{N}{2\pi q(q+N)})$. The first term is the same as we got before, the second is a relatively small correction omitted previously, which however gives a large prefactor when exponentiated: $\Omega(q, N) \approx \sqrt{\frac{N}{2\pi q^2}} (eq/N)^N$. This is the total number of all macrostates available to the combined system. Applying the same approximation to the two subsystems,

$$\Omega(q_A, N_A) \Omega(q_B, N_B) \approx \frac{N/2}{2\pi(q/2)^2} (eq/N)^N \exp[-2N(\delta q/q)^2].$$

Here, we previously had $\Omega(q_A, N_A) \Omega(q_B, N_B) \propto (eq/N)^N \exp[-2N(\delta q/q)^2]$; the prefactor is the new result. Since $\int_{-\infty}^{\infty} \exp[-2N(\delta q/q)^2] d\delta q = \sqrt{\pi q^2/2N}$,

$\int_{-\infty}^{\infty} \Omega(q_A, N_A) \Omega(q_B, N_B) d\delta q \approx \frac{2N}{2\pi q^2} \sqrt{\pi q^2/2N} (eq/N)^N \approx \Omega(q, N)$. We conclude that the number of microstates under the Gaussian peak closely approximates the total number of microstates; most of the states are under the Gaussian, and we are not losing any significant number of microstates in the wings of the distribution.

2.6 Recap

$\Omega(q, N) \approx \sqrt{\frac{N}{2\pi q^2}} (eq/N)^N$ for $q > N$ – extremely fast growth with q . $\Omega(q_A, N_A)\Omega(q_B, N_B)$ – a product of a very steeply growing and a very steeply decaying functions, which has a maximum at $q_A = q_B = Q$ for $N_A = N_B = N/2$. $\Omega(q_A, N_A)\Omega(q_B, N_B) \approx \frac{N}{\pi q^2} [e^2(q/2 + \delta q)(q/2 + \delta q)/(N/2)^2]^{N/2} = \frac{N}{\pi q^2} [e^2(q^2 - 4\delta q^2)/N^2]^{N/2} = \frac{N}{\pi q^2} e^N \exp[N/2 \ln((q^2 - 4\delta q^2)/N^2)] = \frac{N}{\pi q^2} e^N \exp[N \ln(q/N) + N/2 \ln(1 - 4\delta q^2/q^2)] \approx \frac{N}{\pi q^2} e^N (q/N)^N \exp(-2N\delta q^2/q^2)$.

2.7 Temperature

Let us restate our claim about the system A+B reaching the state of maximal multiplicity in terms of the growth of entropy. As a function of U_A , S_A grows, while $S_B(U_B) = S_B(U - U_A)$ falls. At some point, $S = S_A + S_B$ reaches the maximum, where $\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$. Since $\frac{\partial S_B}{\partial U_A} = -\frac{\partial S_B}{\partial U_B}$. Therefore, in equilibrium, $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$. Notice that when U_A is below the equilibrium value, system A tends to receive heat from system B. At the same time. We would conventionally say that $T_A < T_B$. At the same time, $\frac{\partial S_A}{\partial U_A} > \frac{\partial S_B}{\partial U_B}$. Therefore, it is natural to associate T_A with $\frac{\partial U_A}{\partial S_A}$. Check dimensions. A very important remark: in $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, the LHS has only quantities describing A, and the RHS has only quantities describing B, so that T could be introduced that determined the properties of the corresponding subsystem. This structure allows for $T_A = T_C$ if $T_A = T_B$ and $T_B = T_C$. Example: for Einstein solid, $S = Nk \ln(eU/\hbar\omega N)$. $T = 1/\frac{\partial Nk \ln(eU/\hbar\omega N)}{\partial U} = U/Nk$, or $U = NkT$ – in accord with equipartition theorem. We will soon show that for the ideal gas, $S = Nk \ln[\frac{V}{N}(\frac{U}{N})^{3/2}]$, so that $U = \frac{3}{2}NkT$. The coefficient is simply determined by the power of U in the log.

2.8 Entropy of an ideal gas

Consider classical ideal gas in a cubic box $L \times L \times L$. (Ideal: non-interacting. Classical: statistics is not quantum, but the states are quantum.) The particles' states are characterized by momenta, the components of which are quantized: $p_i = \pi\hbar n_i/L$ for standing wave with vanishing wavefunction at the walls. The total energy is $U = \sum_{i=1}^{3N} p_i^2/2m$, where the summation goes over 3 components of momentum for all N particles. Let us introduce $\mathcal{R} = (2mU)^{1/2}L/\pi\hbar$. To find Ω , we need to find all sets of n_i so that $\sum_{i=1}^{3N} n_i^2 = \mathcal{R}^2$. The sets of integer n_i 's represent a grid of points in a $3N$ -dimensional space. Then Ω is the number of these points close to the surface of a hypersphere of radius \mathcal{R} . Since \mathcal{R} may

be non-integer, we will allow some tolerance $\delta\mathcal{R}$; at the end we will see that it is unimportant. Since the points in the grid have a density of 1, this number can be represented as the volume of a hypershell of radius \mathcal{R} to $\mathcal{R} + \delta\mathcal{R}$.

A surface of a hypershell in an m -dimensional space, $S_m(\mathcal{R})$ can be calculated with a trick. Consider any spherically symmetric $f(\mathcal{R})$. We can integrate it over the whole space in two equivalent ways: $\iiint \prod_{i=1}^m dx_i = \int_0^\infty S_m(\mathcal{R})d\mathcal{R}$. Let us choose to integrate

$$f(\mathcal{R}) = \prod_{i=1}^m \exp(-x_i^2) = \exp(-\mathcal{R}^2). \text{ Since } \int \exp(-x^2)dx = \pi^{1/2}, \text{ on the LHS we}$$

$$\text{have } \iiint \prod_{i=1}^m \exp(-x_i^2)dx_i = \pi^{m/2}. \text{ On the RHS we have } \int_0^\infty S_m(\mathcal{R})\exp(-\mathcal{R}^2)d\mathcal{R}. \text{ Since}$$

$$S_m(\mathcal{R}) = S_m(1)\mathcal{R}^{m-1}, \text{ the RHS becomes}$$

$$S_m(1) \int_0^\infty \mathcal{R}^{m-1}\exp(-\mathcal{R}^2)d\mathcal{R} = \frac{1}{2}S_m(1) \int_0^\infty (\mathcal{R}^2)^{m/2-1}\exp(-\mathcal{R}^2)d\mathcal{R}^2 = \frac{1}{2}S_m(1)\Gamma(m/2).$$

Thus, $S_m(\mathcal{R}) = 2\pi^{m/2}\mathcal{R}^{m-1}/\Gamma(m/2)$.

Using this expression, $\Omega = \frac{2\pi^{3N/2}\mathcal{R}^{3N-1}\delta\mathcal{R}}{\Gamma(3N/2)2^{3N}}$. The expression is divided by 2^{3N} because n_i can only be positive. (Negative n_i describe the same standing wave.) Finally, using Stirling's approximation, $\ln \Omega \approx \frac{3N}{2} \ln\left[\frac{\pi e\mathcal{R}^2}{4(3N/2)}\right] + \ln(2\delta\mathcal{R}/\mathcal{R})$. The last term is clearly negligible. Finally, $\ln \Omega \approx N \ln\left[\frac{\pi emU}{3N}\right]^{3/2} \frac{V}{(\pi\hbar)^3}$.

2.9 Free expansion, entropy of mixing, and Gibbs factor

The expression for the entropy seems complicated, but the changes of entropy are easier to interpret. There are several important cases we can consider:

a) Free expansion. Let us say a gas is placed in one half of a container, and then the partition wall is removed, so that $V/2 \rightarrow V$. The gas does not perform any work, so its internal energy does not change, and $S \rightarrow S + Nk \ln 2$. This is an example of an irreversible process – the entropy of a closed system is increased. You would need to apply some manipulations, e.g. by compressing the gas with a piston while cooling it, in order to bring it back to the initial state. The entropy $\Delta S = Nk \ln 2$ is then carried over to the external objects involved in the process – the growth of entropy is irreversible.

b) Entropy of mixing. Suppose we initially have the left side of the container occupied by N_A atoms of gas A, and the right side of the container occupied by N_B atoms of gas B. When the partition is removed, each gas expands to the full volume, resulting in growth of the entropy by $(N_A + N_B) \ln 2$ – the entropy of mixing. This is also an irreversible process – you cannot separate the gasses now without increasing the entropy of the surrounding.

c) However, there is one exception. Namely, if the gasses on the two sides are the same,

one can simply introduce the partition back at any time, and the resulting state would be macroscopically no different from the initial one – it will have $N/2$ atoms on each side of the container. So it would be nice if the expression for the change of entropy gave us zero, rather than $N \ln 2$. Where is the catch? This problem is known as the Gibbs paradox, and the solution, suggested by Gibbs himself, is to treat the atoms as indistinguishable. This is a very natural statement in QM, where the states of the system will be characterized by how many particles occupy a certain energy level, without any distinction of which particle sits on which level. But it was not at all a trivial statement back then – why would not you be able somehow tag the atoms?

With the atoms being indistinguishable, we have to correct our expression for multiplicity: $\Omega = \tilde{\Omega}/N!$, and $S = Nk \ln[\frac{e^{5/2}V}{N}(\frac{4\pi mU}{3h^2N})^{3/2}] \propto Nk \ln[\frac{V}{N}(\frac{U}{N})^{3/2}]$. This expression does not change our conclusion about the entropy change in the free expansion, $\Delta S = Nk \ln 2$. It also results in $\Delta S = 0$ when mixing containers of identical gas: in the initial state we have $S = 2 \cdot N/2k \ln[\text{const} \frac{V/2}{N/2}(\frac{U/2}{N/2})^{3/2}]$, and in the final state we have $S = Nk \ln[\text{const} \frac{V}{N}(\frac{U}{N})^{3/2}]$, which are the same.

Notice that it works now because V enters the expression through the N/V combination, which ensures that S is truly an extensive quantity. Also notice that the entropy of mixing for different gases is still given the expression we got previously:

$$S_{\text{initial}} = N_A k \ln \text{const} [\frac{V/2}{N_A} (\frac{U}{N_A})^{3/2}] + N_B k \ln [\text{const} \frac{V/2}{N_B} (\frac{U}{N_B})^{3/2}], \text{ while}$$

$S_{\text{final}} = N_A k \ln [\text{const} \frac{V}{N_A} (\frac{U}{N_A})^{3/2}] + N_B k \ln [\text{const} \frac{V}{N_B} (\frac{U}{N_B})^{3/2}]$ – we do not get $\ln \frac{V}{N_A + N_B}$ because the atoms are distinguishable – and hence $\Delta S = (N_A + N_B)k \ln 2$.

3 Thermodynamics

3.1 Reversible and irreversible processes

Second law: closed macroscopic system spontaneously tends to macrostates with maximal multiplicity. Or equivalently, since $\Omega \propto e^{S/k}$, their total entropy is always growing. Notice that this is not a fundamental law of nature like Newton's laws, or Maxwell's equations, but a strong statement based on probability arguments.

If a process increases the total entropy, according to the second law it cannot be reversed and hence is called **irreversible**. Similarly, a **reversible** process is the one that does not change the global entropy. Every reversible process must be quasistatic. One can understand this statement by imagining the particles occupying some QM levels, and for a slow enough compression / expansion the particles will stay on their levels so that the multiplicity and entropy will not change. The opposite is not true – a quasistatic process

could be irreversible.

From the definition of temperature, $T = \partial U / \partial S$, it follows that $\Delta S = \Delta U / T$. We have seen earlier that $\Delta U = Q + W$. If the volume does not change, $W = 0$, $\Delta U = Q$ and $\Delta S = Q / T$, which is the original definition of entropy through heat, or $Q = T \Delta S$, which is the way one may define heat now, once entropy is introduced microscopically. [These expressions also work for processes in which the volume changes quasistatically, as we will see later.]

An example of an irreversible process is that of heat transfer between two objects with different T : $\Delta S = \frac{\partial S_A}{\partial U_A} \Delta U - \frac{\partial S_B}{\partial U_B} \Delta U = \Delta U (1/T_A - 1/T_B) > 0$ when ΔU is transferred from hot B to cold A. The only way to avoid this is to have the heat transfer isothermal, with $T_A = T_B$ so that $\Delta S = 0$. (One would have to set an infinitesimally small temperature difference just to ensure the direction of the heat and entropy flow. Upon the reversal of this infinitesimally small difference, the heat and entropy will flow in reverse.) Another reversible process is the quasistatic adiabatic compression/expansion – the isentropic process with $\Delta S = 0$ – that we will see soon.

3.2 Pressure

Imagine two systems at constant total U and separated by a movable partition (constant total V). In equilibrium, the total multiplicity and total entropy must be maximal viewed as a function of two variables, U and V . Maximizing S with respect to U gives us $T_A = T_B$. Variation of S with V : $0 = \left(\frac{\partial S_{total}}{\partial V_A} \right)_U = \left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} + \left(\frac{\partial S_B}{\partial V_A} \right)_{U_B} = \left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B}$, since $\partial V_A = -\partial V_B$ if $V_A + V_B = V_{total}$. So, $\left(\frac{\partial S_A}{\partial V_A} \right)_{U_A} = \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B}$. In equilibrium, the pressures of the two systems should be equal, so it tempting to relate $\left(\frac{\partial S}{\partial V} \right)_U$ with P . In fact, it is equal to P/T . One can see this from dimensionality: $[S/V] = J/Km^3$, while $[P/T] = N/m^2K$. Alternatively, in the ideal gas, where $U \propto T = const$, $P/T = \left(\frac{\partial S}{\partial V} \right)_U = \left(\frac{\partial Nk \ln V}{\partial V} \right)_U = Nk/V$.

Finally, there is the following elegant argument (taken from Kubo's book). Consider a cylinder of gas of height x and area A compressed by a piston with a force F . The multiplicity $\Omega(U, V) = \Omega(U_0 - Fx, V_0 + Ax)$ should be maximal in the equilibrium. Let us look for maximum of $S = k \ln \Omega$ with respect to x : $\frac{\partial S}{\partial x} = \left(\frac{\partial S}{\partial U} \right)_V \frac{\partial U}{\partial x} + \left(\frac{\partial S}{\partial V} \right)_U \frac{\partial V}{\partial x} = -F \left(\frac{\partial S}{\partial U} \right)_V + A \left(\frac{\partial S}{\partial V} \right)_U = 0$. The first term is $-F/T$. Hence $\left(\frac{\partial S}{\partial V} \right)_U = F/TA = P/T$.

3.3 Macroscopic view of entropy and thermodynamic identity

Let us now consider a general system and change its U and V infinitesimally in two consecutive steps. (It is important to change volume quasistatically, so that P is well defined.) Then, $dS = dS_1 + dS_2 = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = dU/T + PdV/T$, or $dU = TdS - PdV$. This expression, known as the thermodynamic identity, replaces $\Delta U = Q + W$ for quasistatic processes. In this case, P is well-defined, $W = -PdV$ and therefore $Q = T\Delta S$. We have already seen this result in the case when $dV = 0$ and the gas did not work. The generalization is that now the volume is now allowed to change, but it has to do it quasistatically.

Is Q always equal to $T\Delta S$? No, because remember that P is defined only for quasistatic processes! Indeed, in the example of an ideal gas, if you pull the piston suddenly out, $Q = 0$ (no heat added through the walls) $W = 0$ (gas does not push on piston) and $\Delta U = 0$ (the energy of the gas does not depend on volume for the non-interacting particles). However, $\Delta S \neq 0$ – new entropy is produced, since this is a free expansion.

Incidentally, we can check what happens if we try to compress a freely expanded gas back to one half of the container. We can do that with a piston, while taking the excess heat to the external reservoir. This needs to be done isothermally, in order not to produce any more entropy. At the end, the gas will return back to the initial state at temperature T in one half of the container, so the work done by the piston, $W = NkT \ln \frac{V_i}{V_f} = NkT \ln 2$ will have to be transferred to the reservoir as heat Q and associated entropy $S = Q/T = Nk \ln 2$ – the same entropy produced in free expansion. The isothermal compression did not add to the entropy and hence was reversible.

Finally, a special case of an adiabatic and quasistatic process is called **isentropic**. Indeed: quasistatic gives $Q = T\Delta S$ and adiabatic gives $Q = 0$, so together $\Delta S = 0$, entropy is constant. For an ideal gas, $S = \text{const}$ is equivalent to the argument of the log to be a constant: $(U/N)^{3/2}V/N = \text{const}$. Since $U \propto T$, this gives $T^{3/2}V = \text{const}$. Since $T \propto PV$, this gives $PV^{5/3} = \text{const}$, as we have seen before.

3.4 Third law of thermodynamics

Let us recall that $C_V = (\partial U/\partial T)_V$ and plug in $\Delta S = \Delta U/T$, so that $C_V = T(\partial S/\partial T)_V$, so that $dS = C_V dT/T$. Integrating, $S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT$. In particular, for $T_i = 0$, we have $S(T) - S(0) = \int_0^T \frac{C_V}{T} dT$. Since the LHS is finite, C_V should tend to zero at $T = 0$ so that the integral converges.

3.5 The Chemical Potential

We can complete our set of mental experiments involving two systems in equilibrium by allowing them to exchange particles. Repeating verbatim the arguments for the exchange of volume, we get $\left(\frac{\partial S_A}{\partial N_A}\right)_{U_A, V_A} = \left(\frac{\partial S_B}{\partial N_B}\right)_{U_B, V_B}$. Notice, that earlier we tacitly assumed $N = \text{const}$ in all the partial derivatives. Now it becomes a variable.

The quantity which is equal in equilibrium with respect to the particle exchange is the chemical potential, defined as $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U, V}$. Which this definition, the thermodynamic identity can be augmented as: $dU = TdS - PdV + \mu dN$.

The chemical potential is crucially important for the establishment of equilibrium between different phases, for chemical processes, and for quantum gases. Unfortunately, we cannot get a good feel of this quantity at this point. Indeed, for the ideal gas, $\mu = -T \left(\partial[Nk \ln[\text{const}_1 \frac{V}{N} (\frac{U}{N})^{3/2}]]/\partial N\right)_{U, V} = -kT \ln[\text{const}_2 \frac{V}{N} (\frac{U}{N})^{3/2}] = -kT \ln[\frac{V}{N} (\frac{2\pi mkT}{h^2})^{3/2}]$. At room temperature, the log is large, resulting in $\mu < 0$ and $|\mu| \gg kT$.

3.6 More on thermodynamic identity

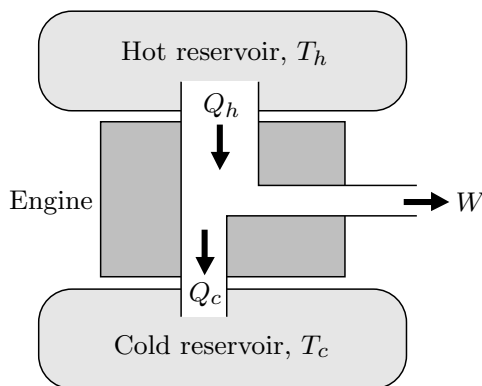
From $dU = TdS - PdV + \mu dN$, it follows that $T = \left(\frac{\partial U}{\partial S}\right)_{V, N}$, $P = -\left(\frac{\partial U}{\partial V}\right)_{S, N}$, and $\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V}$. These expressions are sometimes introduced directly, by starting with $U \equiv U(S, V, N)$ instead of $S \equiv S(U, V, N)$. Indeed, we can solve for U as a function of S . In equilibrium U is minimal as a function of S .

3.7 Gibbs-Duhem equation

One can derive many thermodynamic results using a formal approach, which postulate the existence of an extensive quantity S , which is a function of extensive quantities U , V , and N : $S(U, V, N)$. Solve for U : $U = U(S, V, N)$. Define $T = \left(\frac{\partial U}{\partial S}\right)_{V, N}$, $P = -\left(\frac{\partial U}{\partial V}\right)_{S, N}$, $\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V}$. Then, just by expanding this expression, we get $dU = \left(\frac{\partial U}{\partial S}\right)_{V, N} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N} dV + \left(\frac{\partial U}{\partial N}\right)_{S, V} dN = SdT - PdV + \mu dN$ – the thermodynamic identity.

From the fact that U , V , N , and S are intensive, $U(xS, xV, xN) = xU(S, V, N)$. Take derivative with respect to x at $x = 1$: $U = \left(\frac{\partial U}{\partial S}\right)_{V, N} S + \left(\frac{\partial U}{\partial V}\right)_{S, N} V + \left(\frac{\partial U}{\partial N}\right)_{S, V} N = TS - PV + \mu N$. This is different from the thermodynamic identity! Indeed, it follows that $dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$, from which it follows that $SdT - VdP + Nd\mu = 0$, which is known as the Gibbs-Duhem equation. It tell us that the changes of the three intensive quantities, T , P , and μ are not independent.

Figure 4.1. Energy-flow diagram for a heat engine. Energy enters as heat from the hot reservoir, and leaves both as work and as waste heat expelled to the cold reservoir. Copyright ©2000, Addison-Wesley.



4 Engines

In this section we are going to discuss engines and refrigerators. This is the traditional origin of thermal physics. In order to make some progress, we are often going to assume that all processes are quasistatic.

4.1 Carnot Cycle

An idealized system we will consider consists of a hot reservoir, cold reservoir, and a “heat engine”, which takes the heat from the hot reservoir, performs work, and dumps the heat in the cold reservoir. The reservoirs are assumed to be large enough, and hence having large enough heat capacity, so that their temperature stays constant in the process. The work in this section will be counted from the point of view of the engine, so that the work performed by the engine is positive. The efficiency of the engine will be defined as $e = W/Q_H$ – which percentage of heat is converted into useful work? We will assume that the engine works cyclically, returning at the end of the cycle to the same state as before (same U and S !). From the first law of thermodynamics, $Q_H = Q_C + W$, and $e = (Q_H - Q_C)/Q_H = 1 - Q_C/Q_H$. Unfortunately, one cannot get rid of Q_C , and the efficiency is fundamentally below one. But how high could it be? Recalling that heat and entropy are related, and at best the engine will not produce entropy, the entropy given to the cold reservoir is equal to the entropy taken from the hot reservoir: $S_C \geq S_H \Rightarrow Q_C/T_C \geq Q_H/T_H \Rightarrow Q_C/Q_H \geq T_C/T_H$. Therefore, $e \leq 1 - T_C/T_H$.

It is easy to produce more waste heat and make $S_C > S_H$, but how does one approach the theoretical limit of efficiency? One should avoid producing any new entropy, which means that when the engine exchanges heat with the hot and cold reservoirs, its temperature should be infinitesimally close to theirs. As it absorbs heat from the hot reservoirs, and if its temperature stays constant, it will have to expand, performing work. Similarly,

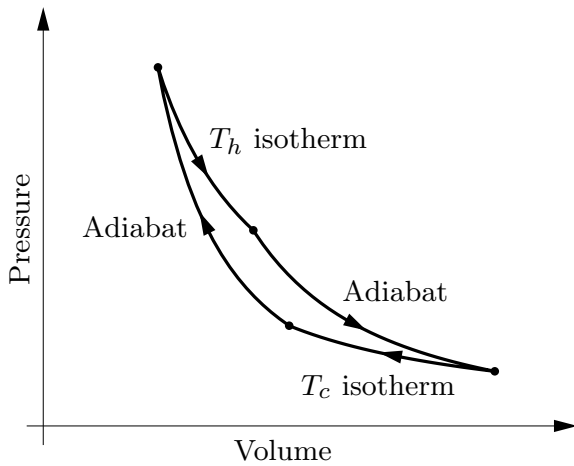


Figure 4.3. PV diagram for an ideal monatomic gas undergoing a Carnot cycle. Copyright ©2000, Addison-Wesley.

when dumping heat in the cold reservoir, it will have to contract. The best one can do in between is to produce no additional entropy, which means that the gas should expand and compress isoentropically. At the end, we obtain the so called Carnot cycle, made of two isotherms and two adiabats. It looks rather odd if one looks at it in the $P - V$ plain, but on the $T - S$ plain it makes more sense. Indeed, $W = \oint P dV = \oint T dS$ (as $\oint dU = 0$, so that the work is the area of the loop, while the waist heat is the area below the loop. $e = (Q_H - Q_C)/Q_H = W/(W + Q_C) = 1/(1 + Q_C/W)$, so we have to minimize Q_C and maximize W , which is achieved by a square loop.

4.2 Real engines

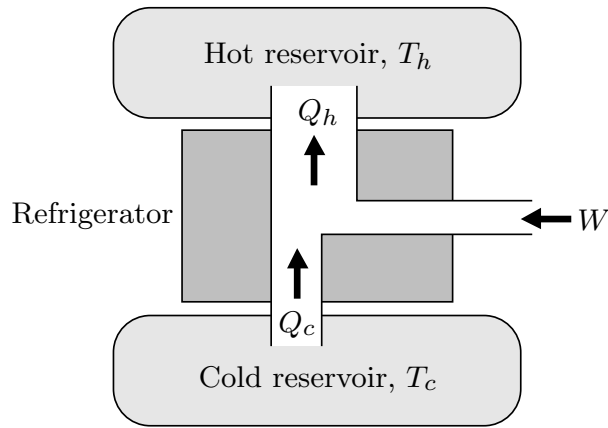
Internal combustion engine can be roughly approximated by the Otto cycle, where the two adiabats are connected by two processes at constant V . One can show that $e = 1 - (V_2/V_1)^{\gamma-1}$, where γ is the adiabatic exponent, $(f + 2)/2$, recall $V^\gamma P = const$. Also, since from the ideal gas law $V^{\gamma-1}T = const$, we can rewrite the efficiency as $e = 1 - (T_1/T_2) = 1 - (T_4/T_3)$, while the efficiency of Carnot cycle between the highest T_3 and lowest T_1 is larger, $e = 1 - (T_1/T_3)$.

One can make the efficiency larger by increasing the compression ratio, V_1/V_2 . Something like that is done in the Diesel cycle, where the air is compressed to become very hot, and ignition is achieved by gradual injection of the fuel.

4.3 Ideal refrigerator

Refrigerator = heat engine operating in reverse. Coefficient of performance, $COP = Q_C/W = Q_C/(Q_H - Q_C) = 1/(Q_H/Q_C - 1)$ could be larger than 1. From the second law, the entropy dumped in the hot reservoir is at least equal to the entropy taken from the cold

Figure 4.4. Energy-flow diagram for a refrigerator or air conditioner. For a kitchen refrigerator, the space inside it is the cold reservoir and the space outside it is the hot reservoir. An electrically powered compressor supplies the work. Copyright ©2000, Addison-Wesley.



reservoir, $Q_H/T_H \geq Q_C/T_C$, so that $COP \leq 1/(T_H/T_C - 1)$. The maximal performance could be achieved by running the Carnot cycle in reverse. The maximal performance could be also argued based on the second law – if one could build the refrigerator with COP exceeding the theoretical limit, one would be able to connect it to the Carnot cycle engine to make a compound engine which produces no waist heat.

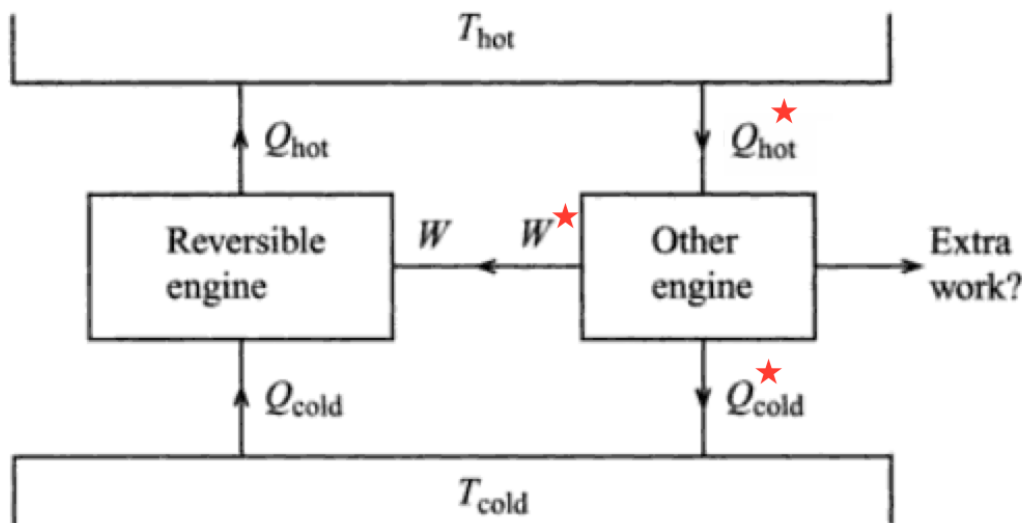
COP can be also written as $COP = T_C/(T_H - T_C)$. We see that the performance falls as T_C becomes lower.

4.4 Second Law – again

Clausius: It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a colder body to a hotter body. Kelvin-Planck: It is impossible to construct a device that operates in a cycle and whose sole effect is to perform work by absorbing heat from a single reservoir.

Carnot theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

One can prove Carnot theorem from either formulation of the second law by assuming that it is possible to create an engine with $e' > e$, or $W'/Q'_H > W/Q_H$. Indeed, connect it to a Carnot cycle operating in reverse. Make Carnot cycle use all energy of the hypothetical engine: $W' = W$. Then, $Q_H > Q'_H$, and $Q_C = Q_H - W > Q'_C = Q'_H - W$. The compound engine does no work, but transfers heat $Q_H - Q'_H = Q_C - Q'_C$ from the cold body to the hot body. This violates the second law in the formulation of Clausius. Alternatively, make $Q'_C = Q_C$. Then $W' > W$ and $Q'_H > Q_H$. The compound engine does work $W' - W$, taking the heat only the hot body. This violates Kelvin-Planck.



5 Phase transitions and thermodynamic potentials

5.1 Thermodynamic potentials

Enthalpy – energy required to create a system with internal energy U and push against the outside pressure P to make it occupy volume V : $H = U + PV$. Introduce two more thermodynamic potentials: Helmholtz free energy: $F = U - TS$ and Gibbs free energy $G = U - TS + PV$. Physical meaning: required to create a system with internal energy U (or enthalpy H) while being able to borrow the heat from the environment with fixed temperature T . Per each ΔS in entropy of the system, we can transfer the amount of heat $T\Delta S$ from the environment, so less energy is required, hence $-TS$.

5.2 Thermodynamic identities

Recall the thermodynamic identity $dU = TdS - PdV + \mu dN$. We can now expand it to include $dH = TdS + VdP + \mu dN$, $dF = -SdT - PdV + \mu dN$ and $dG = -SdT + VdP + \mu dN$. While the equation of state ($PV = NkT$) allows one to express some variables through the others, it is most natural to use the ones that enter the thermodynamic identity as a differential to describe the corresponding potential. So for U , it was best to use S , V and N . Often, T rather than S is given, so F and G are the natural potentials to consider. This procedure is in some sense similar to the change of variables, and is known as Legendre transformation.

5.3 Partial derivatives and Maxwell relations

We had seen $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$, $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$, and $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$. We can now also add $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ and similar for the other potentials. These relations underscore the usefulness of F and G – their partial derivatives are with respect to T or taken at constant T (and not S).

We can also use the fact that the mixed derivatives do not depend on the order. Hence $\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_{V,N}\right)_{T,N} = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,N}\right)_{V,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$.

5.4 Chemical potential

All thermodynamic potentials are extensive. In particular, so is G . Consider $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$. Notice that the derivative is taken at constant intensive quantities. Once can scale the system size and all intensive quantities, including G , keeping all intensive quantities fixed. Then $\left(\frac{\partial G}{\partial N}\right)_{T,P} = G/N$. So $G = \mu N$. We have already seen that $U = TS - PV + \mu N$. This is another way of deriving this relation, since $G = U - TS + PV$.

5.5 Equilibrium

Consider a system in thermal contact with a very large reservoir, whose temperature is constant at T . The total entropy of the system + environment, $S_{tot} = S + S_R$ should be maximal. Since $dS = dU/T + PdV/T - \mu dN/T$, at constant V and N , $dS_R = dU_R/T_R$, or $dS_{tot} = dS + dU_R/T_R$. In equilibrium, $T_R = T$, and $dU + dU_R = 0$, so $dS_{tot} = (dS - dU/T)_T = -dF/T$. Since S_{tot} has to be maximized, F (of the system, not system + environment!) has to be minimized. Similarly, G is maximal for a system in thermal and pressure equilibrium with the environment. It is particularly important in experiments (e.g. chemistry) where P and T are controlled. Finally, H is minimal at constant S and P .

Furthermore, one can show that the max S requirement at constant U and V is equivalent to min U at constant S and V . (Imagine $S = aU - b(X - X_0)^2$. The maximum of S at $U = const$ is at $X = X_0$. Equivalently, we have to look for the maximum of $U = S/a + b/a(X - X_0)^2$ at constant S . Importantly, $a = 1/kT > 0$.)

5.6 Formal structure

Fundamental relation (or equation) $U(S)$. It contains all the information about the system, but is not convenient, because we cannot control S in the lab. So let us find $T(S) =$

$(\frac{\partial U}{\partial S})$, resolve for $S(T)$ and substitute to express $U(T)$. The problem is that knowing this function $U(T)$ does not allow one to uniquely resolve it for $U(S)$. Indeed, $U(T)$ should be viewed as a first order differential equation $U = U(\frac{\partial U}{\partial S})$, which has as solution $S = S(U) + const$. Example: in ideal gas, $S = Nk \ln[const \frac{V}{N} (\frac{U}{N})^{3/2}]$, or $U = const N (\frac{N}{V})^{2/3} \exp(2S/3Nk)$. $T(S) = (\frac{\partial U}{\partial S}) = 2U/3Nk$, or $U = 3NkT/2$. Clearly lots of information about the system is lost – V does not enter any more! (The equation is $U = 3Nk(\frac{\partial U}{\partial S})/2$, so $S = Nk \ln[const U^{3/2}]$; again, V dependence is lost.)

The resolution of this problem is to rewrite the fundamental relation in terms of the thermodynamic potential that is suitable for working with T , $F(T)$. More generally, if we have a fundamental relation $y(x)$, and we want to replace x with $p = dy/dx$ (which is a tangent to the original curve), we have to indicate the position q where this tangent line intercepts the vertical axis at $x = 0$: $y = q + x dy/dx = q + px$, or $q = y - x dy/dx$. Going back, knowing $q(p)$ allows one to reconstruct $y(x)$ without ambiguity. Indeed, $dq = dy - p dx - x dp = -x dp$ (the first terms cancelled since $p = dy/dx$), or $x = -dq/dp$, and $y = q + px = q - pdq/dp$. Notice that the direct and inverse transformations are the same (up to the sign).

Example: ideal gas. Starting with $U = const N (\frac{N}{V})^{2/3} \exp(2S/3Nk)$,

$T(S) = (\frac{\partial U}{\partial S}) = 2/(3Nk) const N (\frac{N}{V})^{2/3} \exp(2S/3Nk)$, which can be resolved for $S = Nk \ln[const \frac{V}{N} (3NkT/2)^{3/2}]$,

$F = U - ST = 3NkT/2 - NkT \ln[const \frac{V}{N} (\frac{3/2NkT}{N})^{3/2}]$ (no need to simplify).

This is a fundamental relation which contains all the information about the system and allows one to reconstruct the original $U(S)$. Indeed, $S = -(\frac{\partial F}{\partial T}) = 3Nk/2 - 3Nk/2 + Nk \ln[const \frac{V}{N} (\frac{3/2NkT}{N})^{3/2}]$. $U = F + TS = 3NkT/2$ (the log terms cancel) and resolving $S(T)$ for $T = 2/(3k)(\frac{N}{V})^{2/3} \exp(2S/3Nk)$ we get the original fundamental relation $U = const N (\frac{N}{V})^{2/3} \exp(2S/3Nk)$.

5.7 Phase Transitions

Phase transition – a discontinuous change of the properties of the substance, caused by an infinitesimal change of external parameters. The different forms of the substance are called phases. Solid-liquid-gas. Critical point, triple point. ^3He , ^4He - no triple point, but a QCP at $T = 0$. Other interesting examples: normal-superconductor, normal-ferromagnet.

First order transitions – first derivative of a thermodynamic potential has a jump. Example: graphite-diamond. For $P = 0$, $G_{gr} < G_{dia}$. $V = (\frac{\partial G}{\partial P})_{T,N}$. Diamond is more dense, so for the same amount, its V is smaller, and G_{dia} becomes lower than G_{gr} at some high P , making the diamond more stable a higher pressures. The slope of G indeed

changes at that point. Also, $S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$. $S_{gr} > S_{dia}$, so the graphite becomes more stable at higher T . Now you would have to apply more P to convert graphite to diamond at high T . So there is a non-trivial phase boundary between graphite and diamond on the $P - T$ plane. The shape of this boundary is determined by $G_{gr} = G_{dia}$.

The slope of the phase separation line in the $P - T$ plane can be determined by condition $dG_1 = dG_2$, or from thermodynamic identity: $-S_1 dT + V_1 dP = -S_2 dT + V_2 dP$ (at constant N), or $\frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2}$. The entropy difference is related to the latent heat of transformation: $L = T\Delta S$, so that $\frac{dP}{dT} = \frac{L}{T\Delta V}$. This is Clausius-Clapeyron relation.

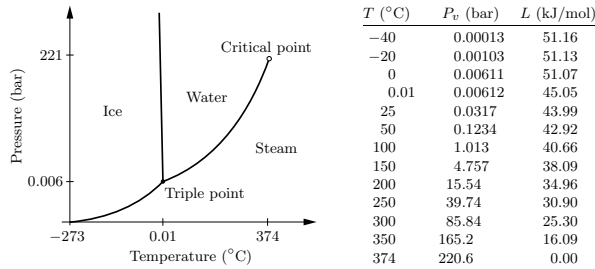


Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994). Copyright ©2000, Addison-Wesley.

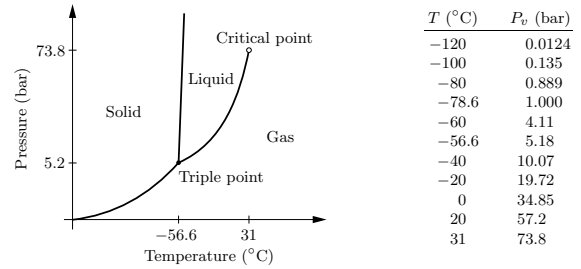


Figure 5.12. Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979). Copyright ©2000, Addison-Wesley.

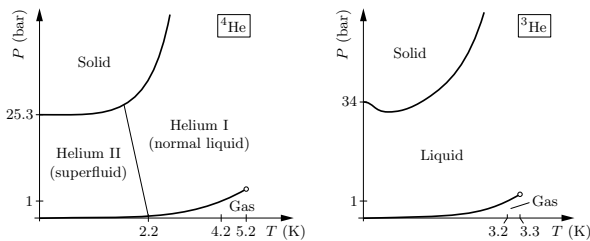


Figure 5.13. Phase diagrams of 4He (left) and 3He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of 3He below 3 mK. Copyright ©2000, Addison-Wesley.

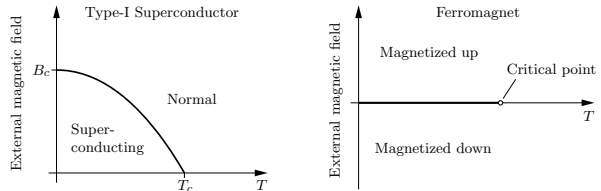


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis. Copyright ©2000, Addison-Wesley.

The high temperature phase must be the more disordered one, so that $-TS$ term in G would stabilize it. Usually, it is also less dense, and the slope of the phase boundary is positive. However, water is heavier than ice (ice floats), so $\frac{dP}{dT}$ is negative. This fact enables ice skating, as pressure induces transition from ice to water at constant T (Callen's book).

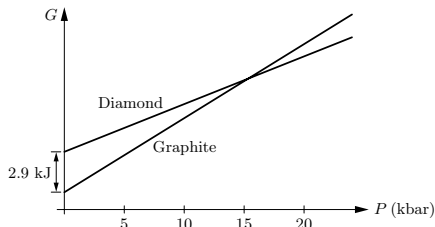


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases. Copyright ©2000, Addison-Wesley.

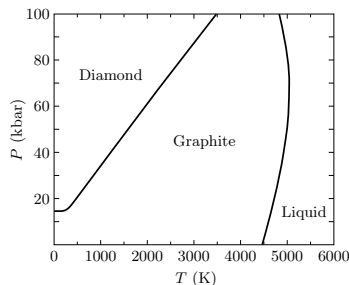


Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991). Copyright ©2000, Addison-Wesley.

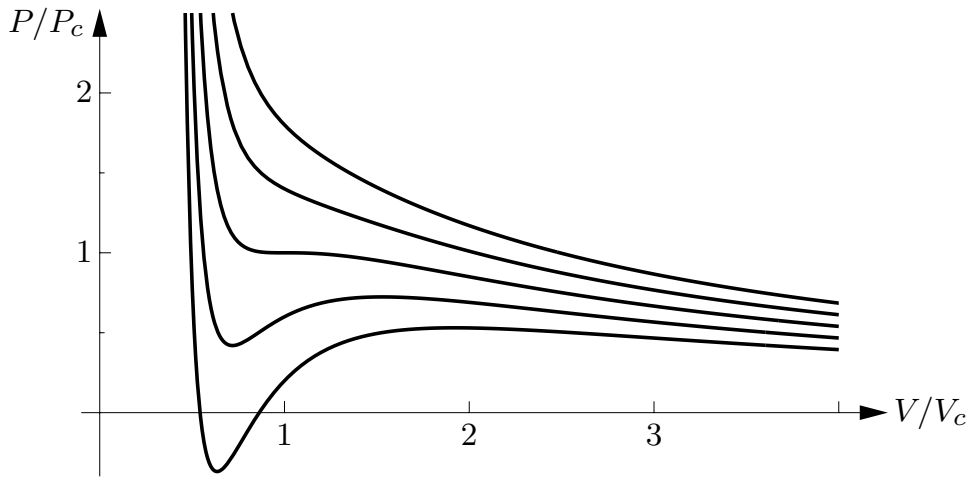


Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c , the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum volume (Nb) is $1/3$. Copyright ©2000, Addison-Wesley.

5.8 van der Waals gas

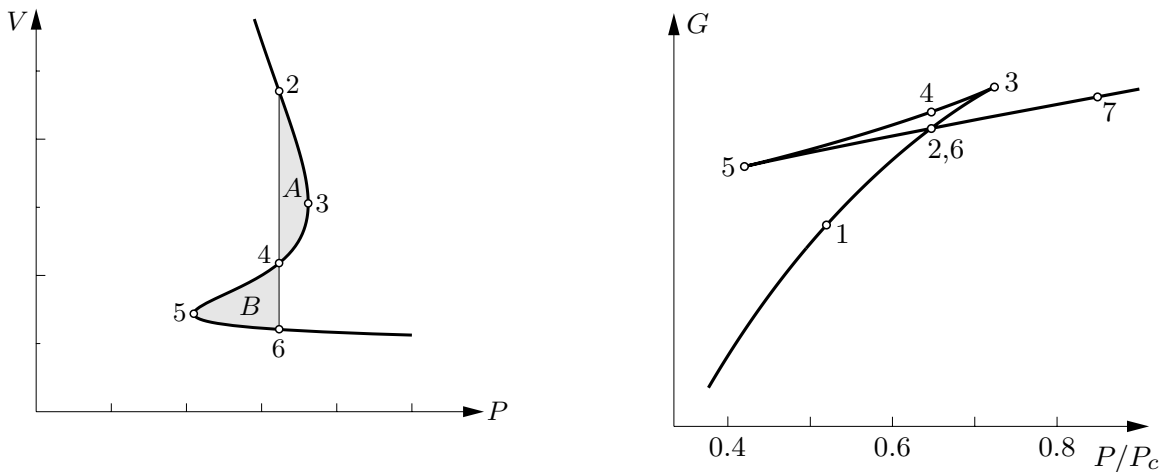
Approximation beyond the ideal gas. Often, atoms or molecules of the gas experience weak attractive (van der Waals) forces when far apart, and strong repulsive forces when brought close together. The repulsive forces, effectively exclude some part of the volume $\propto N$, so the volume enters the equation as $V - bN$. The attraction reduces the (free) energy per particle by an amount proportional to the density of other particles (assuming they do not clump, i.e. there are no correlations between them). Summing over all particles in the system, this gives $\Delta F = -aN^2/V$, which results in $\Delta P = -\left(\frac{\partial \Delta F}{\partial V}\right)_{T,N} = -aN^2/V^2$. As a result, we get $(P + aN^2/V^2)(V - Nb) = NkT$.

The isotherms are shown in Figure 5.20. In particular, there is an isotherm for which there is a point at which $\left(\frac{\partial P}{\partial V}\right)_{T,N} = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N} = 0$. This point occurs at $V_c = 3Nb$, $P_c = a/27b^2$, $kT_c = 8a/27b$. We will show that this is the critical point of this model. We see that $NkT_c/P_c V_c$ has a universal value of $8/3$. (Experimental value is commonly 3.5 – 4.) Introducing $V_r = V/V_c$, $P_r = P/P_c$, $T_r = T/T_c$, we can re-write the vdW equations as $(P_r + 3/V_r^2)(3V_r - 1) = 8kT_r$. All the information about the individual properties of the gas are gone by now, and all gases that obey vdW equation behave universally. This universality is a very common feature of phase transitions. Universality classes. Exponents (problem 5.55).

At the next step, let us discuss the stability of the isotherms shown in the figure. Let us

imagine two identical containers with a substance described by $F(T,V,N)$ that are separated by a movable partition. Imagine a fluctuation of the partition which leads to ΔV . Then, the change of the free energy is $F(T, V + \Delta V, N) + F(T, V - \Delta V, N) - 2F(T, V, N) \approx \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \Delta V^2 = -\left(\frac{\partial P}{\partial V}\right)_{T,N} \Delta V^2$. For stability, F should be minimal, which means $\left(\frac{\partial P}{\partial V}\right)_{T,N} \Delta V^2 < 0$. If some parts of the isotherm do not satisfy this condition, they are unstable. A spontaneous fluctuation will lead to density increasing on one side and decreasing on the other, leading to phase separation.

We see that the vdW gas isotherms have regions that are absolutely unstable, leading to phase separation. Let us analyze the stability and the phase diagram of the vdW gas by plotting $G(P)$ at constant T and N . From the thermodynamic identity, $G = \int V dP$, and we can graphically integrate the isotherm by flipping the graph to read V vs. P . There are several features here. Minimum of G follows 1-2-6-7 line. Point 2, 6 corresponds to the co-existence of gas and liquid. Region 3-4-5 is absolutely unstable, while 2-3 and 5-6 are supersaturated vapor and superheated liquid.



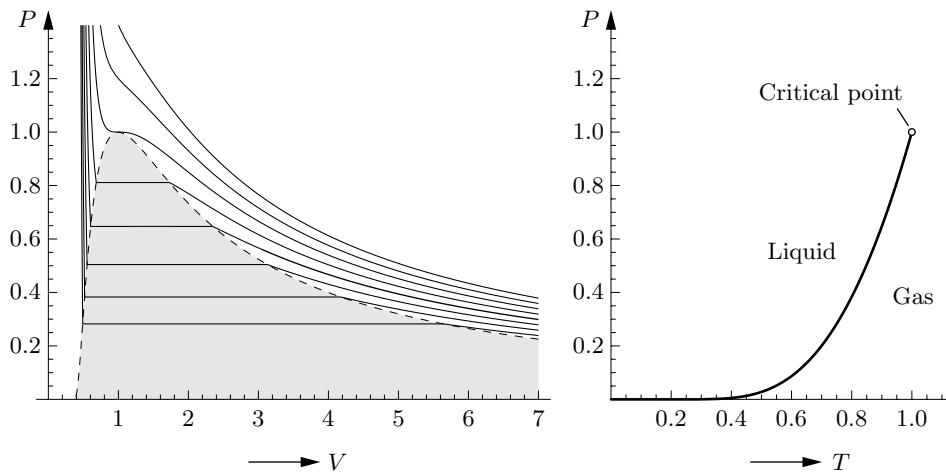


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values. Copyright ©2000, Addison-Wesley.

6 Canonical distribution

6.1 Boltzmann Statistics

We have initially assumed that all states of a system with fixed macroscopic observables (intensive parameters), including energy, are equally probable. This is called microcanonical ensemble. Consider now a system in thermal equilibrium with a reservoir. We will assume that the total of the system and the reservoir is microcanonically distributed. What is the distribution of the system? Let us consider state (i) with energy E . (This is possibly one of many QM states of that energy.) The reservoir has the energy of $E_0 - E_i$, with the number of microstates $\Omega_R(E_0 - E_i)$. The probability of encountering the state (i) is proportional to the number of the microstates of the total (system + reservoir) in which the system is in state (i). There are $\Omega_R(E_0 - E_i)$ such states, so $P_i = \Omega_R(E_0 - E_i)/\Omega_{tot} \propto \exp\{S_R(E_0 - E_i)/k\}$. For a large reservoir, $E_i \ll E_0$, so that we can expand $P_i \propto \exp\{S_R(E_0)/k - \frac{\partial S_R}{\partial E} E_i/k\} \propto \exp\{-E_i/kT\}$. This is Boltzmann or canonical distribution.

Rather than tracing the prefactors, we will normalize P_i in a different way. Since $\sum_i P_i = 1$, we can write $P_i = \frac{\exp(-E_i/kT)}{Z}$, where $Z = \sum_i \exp(-E_i/kT)$. This quantity is known as the “partition function”.

6.2 Connection to Thermal Physics

$U = \langle E_i \rangle = \sum_i E_i P_i = \sum_i E_i \exp(-E_i/kT)/Z$. Let us introduce $\beta = 1/kT$. Then

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial}{\partial \beta} \ln(Z).$$

Example: spin 1/2: $Z = e^{\mu B/kT} + e^{-\mu B/kT} = 2 \cosh(\mu B/kT)$. $U = -\frac{\partial \ln Z}{\partial \beta} = -\mu B \tanh(\mu B/kT)$. Alternatively, $\langle E \rangle = \sum_s E(s) P(s) = (-\mu B) e^{\mu B/kT} + (\mu B) e^{-\mu B/kT} = -\mu B \tanh(\mu B/kT)$. There are two limits: high field, $\mu B \gg kT$, in which case, $U \approx -\mu B$. Alternatively, $\mu B \ll kT$, in which case, $U \approx (\mu B)^2/kT$ (the difference between up and down probability is $\propto \mu B/kT$, and each carries energy of μB).

Notice that if we have N localized spins (no permutations, so no Gibbs factor), and their states are independent of each other, than Z_{tot} factorizes into Z^N . Indeed, for all other spins' orientations being fixed, one spin can be spin up or spin down, contributing a factor of Z . Therefore, in this case $U = N \langle E_s \rangle$, as expected. This is a common mechanism, whereby the intensive nature of the thermodynamic potentials technically follows from the factorization of Z_{tot} into Z^N – more on that later.

Next, $U = F + TS = F - T \frac{\partial F}{\partial T} = -T^2 \frac{\partial(F/T)}{\partial T} = \frac{\partial(\beta F)}{\beta}$. Comparing this with $U = -\frac{\partial}{\partial \beta} \ln(Z)$, we identify $F = -kT \ln Z$. This formula allows one to directly obtain the fundamental relation $F(T, V, N)$ from the knowledge of $Z(T, V, N)$.

Finally, let us consider $\langle \ln P_i \rangle = \langle -\beta E_i - \ln Z \rangle = -\beta(U - F) = (TS)/kT = -S/k$. Therefore, $S = -k \langle \ln P_i \rangle = -k \sum_i P_i \ln P_i$. In fact, this is the most general definition of entropy. Although we derived it here for the canonical ensemble, it holds also for the micro canonical one. Indeed, there all $P_i = 1/\Omega$, so $S = -k \sum_i P_i \ln P_i = -k \Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega$, as we defined previously.

6.3 Example: harmonic oscillator

$Z = \sum_{n=0}^{\infty} e^{-(n+1/2)\beta \hbar \omega} = e^{-\beta \hbar \omega/2} \sum_{n=0}^{\infty} e^{-n\beta \hbar \omega} = e^{-\beta \hbar \omega/2} / (1 - e^{-\beta \hbar \omega})$. $U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{-\partial \beta \hbar \omega/2}{\partial \beta} - \frac{-\partial \ln(1 - e^{-\beta \hbar \omega})}{\partial \beta} = \hbar \omega/2 + \hbar \omega e^{-\beta \hbar \omega} / (1 - e^{-\beta \hbar \omega}) = \hbar \omega (1/2 + \frac{1}{e^{\beta \hbar \omega} - 1})$. Identifying $\hbar \omega/2$ as the zero-point energy, the average number of excitation quanta is $\frac{1}{e^{\beta \hbar \omega} - 1}$, which we will encounter dealing with the blackbody radiation.

Limits: a) If $kT \ll \hbar \Omega$, then $E \approx \hbar \omega (1/2 + e^{-\hbar \omega/kT})$ – exponentially small probability of filling the lowest excited state. b) If $kT \gg \hbar \Omega$, then $E \approx \hbar \omega (1/2 + 1/(1 + \hbar \omega/kT + \dots - 1)) \approx kT$ – this is an example how equipartition is achieved in the classical limit.

$F = -kT \ln Z = \hbar\omega/2 + kT \ln(1 - e^{-\beta\hbar\omega})$. Let us use this result to calculate the entropy: $S = -\left(\frac{\partial F}{\partial T}\right) = -k \ln(1 - e^{-\hbar\omega/kT}) + kT \hbar\omega / kT^2 \frac{e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}} = k[\hbar\omega/kT \frac{e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}} - \ln(1 - e^{-\hbar\omega/kT})]$. From here, one can again get $U = F + TS = \hbar\omega(1/2 + \frac{1}{e^{\hbar\omega/kT} - 1})$.

Finally, heat capacity: $C_V = \left(\frac{\partial(F+TS)}{\partial T}\right) = T \left(\frac{\partial S}{\partial T}\right) = -\beta \left(\frac{\partial S}{\partial \beta}\right) = k(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = k(\hbar\omega/2kT)^2 / \sinh^2(\hbar\omega/2kT)$.

6.4 Fluctuations

Why do the two ensembles give the same results? Let us consider the fluctuations of energy. (Refer back to the figure with the narrow distribution of Ω 's vs. energy for two macroscopic systems in thermal equilibrium.)

Technically: $U = \langle E_i \rangle = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}$; consider

$$\partial U / \partial \beta = -\frac{\sum_i E_i^2 \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} + \left(\frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}\right)^2 = -\langle E_i^2 \rangle + \langle E_i \rangle^2 = -\langle \delta E_i^2 \rangle$$

Indeed, $\langle \delta E_i^2 \rangle \equiv \langle (E_i - \langle E_i \rangle)^2 \rangle = \langle E_i^2 \rangle - 2\langle E_i \rangle^2 + \langle E_i \rangle^2 = \langle E_i^2 \rangle - \langle E_i \rangle^2$.

Next, $\langle \delta E_i^2 \rangle = -\partial U / \partial \beta = -\frac{\partial U}{\partial T} / \frac{\partial \beta}{\partial T} = kT^2 C_V$. Therefore, the relative magnitude of fluctuations $\sqrt{\langle \delta E_i^2 \rangle} / U^2 = \sqrt{kT^2 C_V} / U^2 \approx \sqrt{kT^2 (Nk)} / (NkT)^2 = 1/\sqrt{N}$.

6.5 Detour: Origin of the Ensemble Theory

The word ‘‘ensemble’’ comes from the following idea: instead of watching evolution of a system and averaging observables over time, we could measure the averages over many identical copies of the system – an ensemble – which are in different microstates at a given time. So instead of $\langle f \rangle_{time}$ we want to calculate $\langle f \rangle_{ens}$. Specifically, we want to chose a stationary ensemble, whose distribution in the phase space does not change as the copies of the system involve in time, flowing into each other. Then $\langle f \rangle_{ens} = \langle \langle f \rangle_{ens} \rangle_{time} = \langle \langle f \rangle_{time} \rangle_{ens} = \langle f \rangle_{time}$. The first step $\langle f \rangle_{ens} = \langle \langle f \rangle_{ens} \rangle_{time}$ is true because the ensemble is stationary, and averaging over time does nothing. The second step $\langle \langle f \rangle_{ens} \rangle_{time} = \langle \langle f \rangle_{time} \rangle_{ens}$ is true because the averaging steps (summation over ensemble members and integration over time) can be interchanged. The last step $\langle \langle f \rangle_{time} \rangle_{ens} = \langle f \rangle_{time}$ is generally not true. The assumption is known as ergodicity hypothesis, which roughly states that a system over time will evolve through all microstates, in which case the time average of its properties is the same as the time average of the properties for the other members of the ensemble. This is not true because in some systems some or all members of the ensemble may evolve differently in time. However,

for typical systems that we consider, such that the ideal gas with occasional collisions, $\langle f \rangle_{ens} = \langle f \rangle_{time}$. Finally, one should realize that the number of microstates Ω is so large, that the averaging occurs not because the system probes them all in the course of its time evolution, but because it moves through some small fraction of Ω that is representative of the whole.

6.6 Maxwell-Boltzmann distribution

Consider one molecule in the ideal gas as a system in thermal equilibrium with all the rest. Then $P(\bar{v}) \propto \exp(-m\bar{v}^2/2kT)$. Here \bar{v} is velocity – a 3D vector. If we want to find a distribution probability of the (scalar) speed v , d^3v should be replaced by $4\pi v^2 dv$. The probability becomes $P(v) \propto v^2 \exp(-mv^2/2kT)$. One can immediately see that $\langle v^2 \rangle = \int v^2 P(v) dv / \int P(v) dv \propto kT/m$.

The prefactor could be found from normalization $\int_0^\infty P(v) dv = 1$. Since $\int_0^\infty x^2 e^{-x^2} dx = \sqrt{\pi}/4$, $P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 \exp(-mv^2/2kT)$.

6.7 Distribution for classical systems

Let us consider a classical ideal gas in a box $L \times L \times L$, and characterize the states by their (quantized) momenta of all particles. $Z = \sum_{\text{all } \{p_i\}} \exp(-\sum_{i=0}^{3N} \beta p_i^2/2m)$. The first sum is over all sets of momenta $\{p_i\}$ of all particles. Let us focus on one momentum p_i . It's quantized in units of $\pi\hbar/L$, so

$$\sum_{p_i} = \int_{-\infty}^{+\infty} dp / (2\pi\hbar/L) = L/h \int_{-\infty}^{+\infty} dp$$

(factor 2 in the denominator allows us to extend the integral to $\pm\infty$. Then

$$Z = (L/h)^{3N} \iiint_{-\infty}^{+\infty} \exp(-\sum_{i=0}^{3N} \beta p_i^2/2m) \prod_{i=1}^{3N} dp_i$$

Notice, that since $\exp(-\sum_{i=0}^{3N} \beta p_i^2/2m) = \prod_{i=1}^{3N} \exp(-\beta p_i^2/2m)$, the integral factorizes into a product of $3N$ individual integrals $\int_{-\infty}^{+\infty} \exp(-\beta p_i^2/2m) dp_i = \sqrt{2\pi mkT}$. We can

also group the terms corresponding to p_x, p_y, p_z of one particle to write

$$Z_1 = V(2\pi mkT/h^2)^{3/2} \equiv V/\lambda_T^3$$

where $\lambda_T = h/\sqrt{2\pi mkT}$. Since the thermal momentum of a particle is $\sim \sqrt{mkT}$, λ_T represents the size of the wave packet that can be constructed from the momenta of the order of the thermal one or smaller. The physical meaning of Z_1 is then the number of ways such a packet could fit into the volume V .

In the final step, we introduce the Gibbs factor, to get $Z_N = Z_1^N/N!$.

6.8 Thermodynamics

$$F = -kT \ln(Z_N) \approx -NkT \ln\left(\frac{eV}{Nh^3}(2\pi mkT)^{3/2}\right).$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = NkT/V, \text{ as it should be.}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk \ln\left(\frac{eV}{Nh^3}(2\pi mkT)^{3/2}\right) + 3NkT/2T.$$

$$U = F + TS = 3NkT/2 \text{ (the logarithms cancel.)}$$

6.9 Grand Canonical Distribution and Thermodynamics

Derivation of the GCD, Z_μ and thermodynamics.

6.10 Equipartition theorem

Let us calculate the average energy of a classical system with a Hamiltonian H :

$$U = \frac{\iiint H \exp(-\beta H) \prod_{i=1}^{3N} dr_i dp_i}{\iiint \exp(-\beta H) \prod_{i=1}^{3N} dr_i dp_i}$$

We do not have to normalize the integrals (that would be easy: just by divide them by h^{3N}) as long as the prefactor is the same in the numerator and the denominator, which is the partition function. Let us assume now that the Hamiltonian of the system contains a sum of terms quadratic in coordinates and momenta $H = \sum_{i=0}^{3N} A_i r_i^2 + B_i p_i^2$. The energy is then

$$U = \frac{\iiint \sum_{i=0}^{3N} (A_i r_i^2 + B_i p_i^2) \exp(-\beta H) \prod_{i=1}^{3N} dr_i dp_i}{\iiint \exp(-\beta H) \prod_{i=1}^{3N} dr_i dp_i}.$$

For each term in the sum, the integral factorizes into multiple integrals identical in the numerator and the denominator, which all cancel except for one involving a specific r_i or p_i ; it looks like $\frac{\int Ar^2 \exp(-\beta Ar^2) dr}{\int \exp(-\beta Ar^2) dr} = kT/2$. (Indeed, the dimension of the Ar^2 , according to the exponents, should be $1/\beta$; factor $1/2$ comes from integrating by parts $\int x^2 e^{-x^2} dx = \int e^{-x^2} dx/2$.) Overall, $U = NfkT/2$, where f is the number of the non-zero A 's and B 's per particle.

6.11 Contribution of discrete atomic levels to heat capacity

Atomic levels are split by the spin-orbit interaction into the “fine structure”. Total orbital momentum, $J = L + S$. $Z_{int} = \sum_J (2J + 1) \exp(-\beta E_J)$. At $T = 0$, $Z_{int} = (2J_0 + 1)$ – the degeneracy of the lowest multiplet. When $kT \gg$ all level spacings, $Z_{int} = (2S + 1)(2J + 1)$ – total number of levels available for the given L and S . The energy, being \propto the minus derivative of Z , $U = -\partial \ln Z / \partial \beta$, drops with β – grows with T from 0 to the weighted average of level energies, $U = \sum_J (2J + 1) E_J \exp(-\beta E_J) / Z$. Correspondingly, the heat capacity goes from 0 through a maximum back to 0.

Alternatively, we could look at F and S : $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\partial F + TS}{\partial T}\right)_{V,N} = \left(\frac{\partial F}{\partial T}\right)_{V,N} + S + T \left(\frac{\partial S}{\partial T}\right)_{V,N}$. Since $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, the first two terms cancel, and $C_V = T \left(\frac{\partial S}{\partial T}\right)_{V,N}$. The entropy changes from $Nk \ln(2J_0 + 1)$ at zero temperature to $Nk \ln[(2S + 1)(2J + 1)]$ at high temperature; its derivative has to go to zero at both limits, with a positive bump in the middle, when $kT \sim E_J$.

Physical interpretation: the internal degrees of freedom get activated when $kT \sim E_J$, which requires extra energy, and then, when these degrees of freedom are saturated $kT \gg E_J$, no new energy is need to heat the system further. Note: this contribution is additive to the translational contribution, $3NkT/2$.

6.12 Diatomic molecules

For vibrations, see Sec. 6.3 above. Rotations:

7 Quantum Statistics

7.1 Level occupation

Similar to the number of microstates, Ω , partition function Z_N counts the number of ways to position the particles in the their levels. Gibbs factor $1/N!$ was introduced when

all particles occupied different levels. If the particles could occupy the same level, it no longer works. For examples, 2 particles that can occupy the same level could be distributed between 3 levels in 6 different ways; $3^2/2! = 4.5$ gives a wrong answer, since all double occupancy cases were artificially divided by a factor of 2. Multiple occupancy is not a problem if the number of levels $\sim Z_1$ greatly exceeds N , but becomes an issue when it is comparable with N : $V/\lambda_T^3 \sim N$, or density $n \sim \lambda_T^{-3}$. This happens at low T or high n .

We now switch to characterizing the state of the system by specifying the occupation n_i of each level i , rather than specifying which level a particle occupies. Let us consider the level as a subsystem in equilibrium with other levels. Then $Z_\mu^{(i)} = \sum_{\text{all allowed } n_i} \exp(-\beta n_i(\epsilon_i - \mu))$ and $\Omega^{(i)} = -kT \ln Z_\mu^{(i)}$. For the complete system, $Z_\mu = \prod_i Z_\mu^{(i)}$, and $\Omega = \sum_i \Omega^{(i)}$.

Probability of n_i particles occupying the level is $P(n_i) = \exp(-\beta n_i(\epsilon_i - \mu))/Z_\mu^{(i)}$. The average number of particles per level is $\langle n_i \rangle = \sum_i n_i \exp(-\beta n_i(\epsilon_i - \mu))/Z_\mu^{(i)}$. In a classical gas, $P(0) \approx 1$, $P(1) \approx \exp(-\beta(\epsilon_i - \mu)) \ll 1$, $P(2) \ll P(1)$, and $Z_\mu^{(i)} \approx 1$, so that $\langle n_i \rangle \approx \exp(-\beta(\epsilon_i - \mu))$ – the Boltzmann distribution. The requirement for $\langle n_i \rangle \ll 1$ is the most stringent for $\epsilon_i = 0$, and requires $\exp(\beta\mu) \ll 1$. Recalling that in the classical gas $\mu = -kT \ln[\frac{V}{N}(\frac{2\pi mkT}{h^2})^{3/2}] = kT \ln(n\lambda_T^3)$, we get $\exp(\beta\mu) = n\lambda_T^3$. We again see that the classical statistics works if $n\lambda_T^3 \ll 1$.

7.2 Bosons & Fermions

For particles with the integer spin, the bosons, all values of n_i are allowed. $Z_\mu^{(i)} = \sum_{n_i=0}^{\infty} \exp(-\beta n_i(\epsilon_i - \mu)) = [1 - \exp(-\beta(\epsilon_i - \mu))]^{-1}$. $\langle n_i \rangle = \sum_{n_i=0}^{\infty} n_i \exp(-\beta n_i(\epsilon_i - \mu))/Z_\mu^{(i)} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln(Z_\mu^{(i)}) = \frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln[1 - \exp(-\beta(\epsilon_i - \mu))] = \frac{\beta}{\beta} \frac{\exp(-\beta(\epsilon_i - \mu))}{1 - \exp(-\beta(\epsilon_i - \mu))} = [\exp(\beta(\epsilon_i - \mu)) - 1]^{-1}$.

For particles with the half-integer spin, the fermions, n_i could only be 0 or 1. $Z_\mu^{(i)} = 1 + \exp(-\beta(\epsilon_i - \mu))$ and $\langle n_i \rangle = [0 \times 1 + 1 \times \exp(-\beta(\epsilon_i - \mu))]/Z_\mu^{(i)} = [\exp(\beta(\epsilon_i - \mu)) + 1]^{-1}$.

Both expression could be combined to $n(\epsilon) = [\exp(\beta(\epsilon - \mu)) \pm 1]^{-1}$, where we dropped the averaging sign and i . The expressions approximately reduce to the Boltzmann distribution if $\exp(\beta(\epsilon - \mu)) \gg 1$.

7.3 Quantum corrections to μ in an ideal gas

$N = \sum_i n_i$. Here, the states i can be characterized by the possible quantized values

of the momentum for 1 particle: $\sum_i = \sum_{p_x, p_y, p_z} = \iiint_{-\infty}^{+\infty} d^3p / (2\pi\hbar/L)^3 = V/h^3 \iiint_{-\infty}^{+\infty} d^3p$.

The integrand n_i depends on the energy $\epsilon(p) = p^2/2m$. Let us rewrite $d^3p = 4\pi p^2 dp$ as $d^3p = 4\pi(2m^3\epsilon)^{1/2} d\epsilon$. Then, $\sum_{p_x, p_y, p_z} = V/h^3 \int_0^{+\infty} 4\pi(2m^3\epsilon)^{1/2} d\epsilon \equiv \int_0^{\infty} \nu(\epsilon) d\epsilon$, where

$\nu(\epsilon) = \frac{4\pi V(2m^3\epsilon)^{1/2}}{h^3} \equiv \frac{V(2m^3\epsilon)^{1/2}}{2\pi^2\hbar^3}$ is the ‘‘density of states’’. In case of degeneracy g (e.g. spin), ν has to be multiplied by g . It is important that in the 3-dimensional case with parabolic dispersion, $\nu(\epsilon) = C_1 V \sqrt{\epsilon}$. Therefore,

$$N = \int_0^{\infty} \nu(\epsilon) n(\epsilon) d\epsilon = \int_0^{\infty} C_1 V \epsilon^{1/2} \frac{1}{\exp(\beta(\epsilon - \mu)) \pm 1} d\epsilon$$

If the gas is classical, we can neglect 1 in the denominator, $N \approx \int_0^{\infty} C_1 V \epsilon^{1/2} e^{-\beta(\epsilon - \mu)} d\epsilon = C_1 V e^{\beta\mu} \int_0^{\infty} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon = C_1 V e^{\beta\mu} \frac{\sqrt{\pi}}{2} (kT)^{3/2} = \frac{\sqrt{\pi}}{2} \frac{4\pi(2m^3)^{1/2}}{h^3} V e^{\beta\mu} (kT)^{3/2} = (2\pi m kT)^{3/2} V e^{\beta\mu} / h^3$, and $e^{\beta\mu} = n \lambda_T^3$.

If gas is weakly quantum, $\exp(\beta\mu) \ll 1$, we can approximate $\frac{1}{\exp(\beta(\epsilon - \mu)) \pm 1} \approx \exp(-\beta(\epsilon - \mu)) \mp \exp(-2\beta(\epsilon - \mu))$. Then, $N \approx \int_0^{\infty} C_1 V \epsilon^{1/2} \exp(-\beta(\epsilon - \mu)) d\epsilon \mp \int_0^{\infty} C_1 V \epsilon^{1/2} \exp(-2\beta(\epsilon - \mu)) d\epsilon$. The first integral gives the classical result $N = V \lambda_T^{-3} \exp(\beta\mu)$. The \pm corrections involves an identical integral with twice β , which gives $N = V \lambda_T^{-3} \exp(\beta\mu) [1 \mp 2^{-3/2} \exp(\beta\mu)]$, from which $\exp(\beta\mu) = n \lambda_T^{-3} / [1 \mp 2^{-3/2} \exp(\beta\mu)] \approx n \lambda_T^3 / (1 \mp 2^{-3/2} n \lambda_T^3) \approx n \lambda_T^3 (1 \pm 2^{-3/2} n \lambda_T^3)$. (We plug $\exp(\beta\mu) \approx n \lambda_T^3$ in the correction term.) For fermions / bosons, μ is higher / lower than dictated by the classical (Boltzmann) expression.

7.4 Thermodynamics

$PV = -\Omega = kT \ln Z_\mu = kT \ln \prod_i Z_\mu^{(i)} = kT \sum_i \ln Z_\mu^i = \pm kT \sum_i \ln[1 \pm e^{-\beta(\epsilon_i - \mu)}] = \pm kT \int \nu(\epsilon) \ln[1 \pm e^{-\beta(\epsilon - \mu)}] d\epsilon$. Let us take $\nu(\epsilon) = C_1 V \sqrt{\epsilon}$. By parts:

$$PV = \pm kTC_1 V \int \sqrt{\epsilon} \ln[1 \pm e^{-\beta(\epsilon - \mu)}] d\epsilon = \pm kTC_1 V \int \frac{2}{3} \epsilon^{3/2} \frac{\pm \beta e^{-\beta(\epsilon - \mu)}}{1 \pm e^{-\beta(\epsilon - \mu)}} d\epsilon =$$

$$\frac{2}{3} \int \nu(\epsilon) \epsilon \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1} d\epsilon = \frac{2}{3} U$$

However, $PV = NkT$ and $U = 3NkT/2$ are no longer true.

Let us find small corrections to $PV = NkT$ for weakly non-classical gas. Expanding $n(\epsilon) \approx 1 \mp e^{-\beta(\epsilon-\mu)}$, we get

$$\begin{aligned} PV &\approx \frac{2}{3} C_1 V \int \epsilon^{3/2} e^{-\beta(\epsilon-\mu)} (1 \mp e^{-\beta(\epsilon-\mu)}) d\epsilon = \frac{2}{3} C_1 V e^{\beta\mu} \int \epsilon^{3/2} e^{-\beta\epsilon} d\epsilon \mp \\ &\frac{2}{3} e^{2\beta\mu} C_1 V \int \epsilon^{3/2} e^{-2\beta\epsilon} d\epsilon = \frac{2}{3} C_1 V \Gamma(5/2) [e^{\beta\mu} \beta^{-5/2} \mp e^{2\beta\mu} (2\beta)^{-5/2}] = \\ &\frac{2}{3} C_1 V \Gamma(5/2) e^{\beta\mu} \beta^{-5/2} (1 \mp 2^{-5/2} e^{\beta\mu}) \end{aligned}$$

where $\Gamma(5/2) = 3\sqrt{\pi}/4$. Plugging in $\exp(\beta\mu) \approx n\lambda_T^3 (1 \pm 2^{-3/2} n\lambda_T^3)$, we get $P \approx nkT (1 \pm 2^{-3/2} n\lambda_T^3) (1 \mp 2^{-5/2} n\lambda_T^3) \approx nkT (1 \pm 2^{-5/2} n\lambda_T^3)$. As a result, P is higher for fermions (Pauli exclusion pushes particles to the levels with higher momenta) and lower for bosons.

7.5 Fermions

We have seen that $\nu(\epsilon) \propto \epsilon^{1/2}$. Let us write it as $\nu = g\epsilon^{1/2}$. Since $N = \int_0^{\epsilon_F} \nu(\epsilon) d\epsilon = \frac{2}{3} g\epsilon_F^{3/2}$, $g = \frac{3}{2} N/\epsilon_F$. Let us calculate corrections to the chemical potential when $kT \ll \epsilon_F$. The number of particles in the system is independent of temperature, and given by: $N = \int_0^{\infty} \nu(\epsilon) n_{FD}(\epsilon) d\epsilon$. Let us develop a general method of calculating the integrals of this form (Sommerfeld expansion):

Consider $I(\mu, T) = \int_0^{\infty} f(\epsilon) n_{FD}(\epsilon) d\epsilon$. Integrating by parts, $I(\mu, T) = n_{FD}(\epsilon) F(\epsilon) \Big|_0^{\infty} - \int_0^{\infty} F(\epsilon) \frac{dn_{FD}(\epsilon)}{d\epsilon} d\epsilon$, where $F(\epsilon) = \int_0^{\epsilon} f(\epsilon') d\epsilon'$. For power-law $f(\epsilon)$, the first term is equal to zero at both limits (n_{FD} is exponentially small at large ϵ). Here, $-\frac{dn_{FD}(\epsilon)}{d\epsilon} = \frac{1}{kT} \frac{e^{(\epsilon-\mu)/kT}}{(e^{(\epsilon-\mu)/kT} + 1)^2} = \frac{1}{4kT \cosh^2[(\epsilon-\mu)/2kT]}$. This function is symmetric in $\epsilon - \mu$, has width of $\epsilon - \mu \sim kT$ and height $\sim 1/kT$. In fact, it tends to $\delta(\epsilon - \mu)$ in the zero T limit – indeed, then $\left(-\frac{dn_{FD}(\epsilon)}{d\epsilon}\right)$ is a derivative of a step function. Keeping this in mind, we can expand $F(\epsilon)$ in Taylor series: $F(\epsilon) = F(\mu) + f(\mu)(\epsilon - \mu) + f'(\mu)(\epsilon - \mu)^2/2$. We can also expand the limit of integration over ϵ to $-\infty$. Then $I(\mu, T) \approx \int_{-\infty}^{\infty} [F(\mu) + f(\mu)(\epsilon - \mu) + f'(\mu)(\epsilon - \mu)^2/2] \left(-\frac{dn_{FD}(\epsilon)}{d\epsilon}\right) d\epsilon$.

Odd terms in the Taylor series give zero, because $\left(-\frac{dn_{FD}(\epsilon)}{d\epsilon}\right)$ is even with respect to $\epsilon - \mu$.

Using $\int_{-\infty}^{\infty} \frac{x^2}{4 \cosh^2(x/2)} dx = \pi^2/3$ we finally get $I(\mu, T) = F(\mu) + \frac{\pi^2}{6}(kT)^2 f'(\mu)$. Notice that $F(\mu) = \int_0^{\mu} f(\epsilon) d\epsilon$ is formally equal to the unphysical $I(\mu, 0)$.

Applying this to $f = \nu$, we get $N = \int_0^{\mu} \nu(\epsilon) d\epsilon + \frac{\pi^2}{6}(kT)^2 \nu'(\mu)$. On the other hand, at $T = 0$, $N = \int_0^{\epsilon_F} \nu(\epsilon) d\epsilon$. Therefore, $\int_0^{\epsilon_F} \nu(\epsilon) d\epsilon - \int_0^{\mu} \nu(\epsilon) d\epsilon = \frac{\pi^2}{6}(kT)^2 \nu'(\mu)$. The difference between the two integrals is $\approx \nu(\epsilon_F)(\epsilon_F - \mu)$. (It is OK to evaluate ν at ϵ_F , and not at $(\epsilon_F + \mu)/2$ with this precision.) Finally, $\mu \approx \epsilon_F - \frac{\pi^2}{6}(kT)^2 \frac{\nu'(\epsilon_F)}{\nu(\epsilon_F)}$. (Again, we can take ν' at ϵ_F , and not at μ with this precision.) Finally, for $\nu(\epsilon) \propto \epsilon^{1/2}$, $\frac{\nu'(\epsilon_F)}{\nu(\epsilon_F)} = \frac{1}{2\epsilon_F}$ and $\mu \approx \epsilon_F - \frac{\pi^2}{12}(kT)^2/\epsilon_F$.

Taking $U = \int_0^{\infty} \nu(\epsilon) n_{FD}(\epsilon) \epsilon d\epsilon$, so that $f = \epsilon \nu$, we get $U = \int_0^{\mu} \nu(\epsilon) \epsilon d\epsilon + \frac{\pi^2}{6}(kT)^2 (\epsilon \nu)' \approx \int_0^{\epsilon_F} \nu(\epsilon) \epsilon d\epsilon + (\mu - \epsilon_F) \nu(\epsilon_F) \epsilon_F + \frac{\pi^2}{6}(kT)^2 (\epsilon_F \nu' + \nu)$. Second term is equal to $-\frac{\pi^2}{6}(kT)^2 \epsilon_F \nu'$ and cancels with the corresponding part of the third term, leaving $U(T) \approx U(0) + \frac{\pi^2}{6}(kT)^2 \nu(\epsilon_F) = U(T) + \frac{\pi^2}{4}(kT)^2 N/\epsilon_F$, where $\nu(\epsilon_F) = \frac{3N}{2\epsilon_F}$ is substituted.

7.6 Degeneracy pressure

Let us compare $U(T = 0) = \int_0^{\epsilon_F} \nu(\epsilon) \epsilon d\epsilon = C_1 V \int_0^{\epsilon_F} \sqrt{\epsilon} \epsilon d\epsilon = 2C_1 V \epsilon_F^{5/2}/5$ and $N = \int_0^{\epsilon_F} \nu(\epsilon) d\epsilon = C_1 V \int_0^{\epsilon_F} \sqrt{\epsilon} d\epsilon = 2C_1 V \epsilon_F^{3/2}/3$. As a result, $U(T = 0) = 3N \epsilon_F/5$. We get this finite energy at zero temperature because the fermions are forced by the Pauli exclusion to fill the states with nonzero energies. (All the way from zero to ϵ_F – hence the average energy is $U/N \sim \epsilon_F$.) Associated with this energy is a pressure $P = -\left(\frac{\partial U}{\partial V}\right)_{S, N}$. At zero temperature, $S = 0$ (single non-degenerate ground state). Since $\epsilon_F \propto n^{2/3}$, $P = 2U/3V = 2n\epsilon_F/5 \propto n^{5/3}$.

Let us now do a similar calculation for the relativistic particle, $\epsilon = cp$. Since $d^3p = 4\pi p^2 dp = 4\pi \epsilon^2 d\epsilon/c^3$, we see that $\nu(\epsilon) \propto \epsilon^2$. Let us write it as $\nu(\epsilon) = C_2 V \epsilon^2$. $U(T = 0) = \int_0^{\epsilon_F} \nu(\epsilon) \epsilon d\epsilon = C_2 V \int_0^{\epsilon_F} \epsilon^2 \epsilon d\epsilon = C_2 V \epsilon_F^4/4$ and $N = \int_0^{\epsilon_F} \nu(\epsilon) d\epsilon = C_2 V \int_0^{\epsilon_F} \epsilon^2 d\epsilon = C_2 V \epsilon_F^3/3$. We still have $U(T = 0) \sim N \epsilon_F$ (with a different numerical coefficient, 3/4), but $\epsilon_F \propto$

$n^{1/3}$, so that $P \propto n^{4/3}$. This difference between an exponent of $5/3$ and $4/3$ between the non-relativistic and relativistic case will be important in the next section.

7.7 Stability of stars

White dwarf. $U_{gr} = -GM^2/R$. $U_{kin} = \frac{3N\epsilon_F}{5} \sim N \frac{h^2}{m_e} \left(\frac{N}{V}\right)^{2/3}$. Express N through the mass of the star: $\sim M/m_p$ and $V \sim R^3$. Then $U_{kin} \sim \left(\frac{M}{m_p}\right)^{5/3} \frac{h^2}{m_e R^2}$. At small R , kinetic energy becomes larger than potential, stabilizing the star against collapse. The equilibrium is determined by $\frac{dU}{dR} = 0$: $R_0 \sim \left(\frac{M}{m_p}\right)^{5/3} \frac{h^2}{m_e GM^2} = \frac{h^2}{m_e m_p^{5/3} GM^{1/3}}$. The size of the star decreases with M !

For $M \sim M_{solar}$, $R_0 \sim 10^4 km$ (the size of Earth), and $\rho \sim 10^6 kg/m^3$! At the same time $\epsilon_F \sim 10^9 K \sim 10^5 eV$. Note that this value is comparable with $m_e c^2 = 0.5 MeV$. Therefore, eventually at high enough star mass, we have to switch to relativistic energy dispersion: $\epsilon_F = cp_F$. The kinetic energy becomes $U_{kin} \sim Nch\left(\frac{N}{V}\right)^{1/3} \sim \left(\frac{M}{m_p}\right)^{4/3} \frac{hc}{R}$. This expression has the same $1/R$ dependence as the gravitational attraction. The system becomes unstable if $\frac{GM^2}{R} > \left(\frac{M}{m_p}\right)^{4/3} \frac{hc}{R}$, or $M^{2/3} > \frac{hc}{Gm_p^{4/3}}$. The critical value $M_1 = \left(\frac{hc}{G}\right)^{2/3} \frac{1}{m_p^2} \approx 1.4M_{solar}$. Heavier stars collapse, with high pressure forcing inverse β -decay: $e + p = n + \nu$. The result is a neutron star, with a radius $\frac{h^2}{m_p^{8/3} GM^{1/3}}$ – here simply replace m_e with $m_p \approx m_n$. For $M \sim M_{solar}$, $R_0 \sim 10 km$, and $\rho \sim 10^{17} kg/m^3$ – comparable to a density of an atomic nucleus! $\epsilon_F \sim 10^{11-12} K \sim 10^{7-8} eV$. Since $m_p c^2 \sim 10^9 eV$, the system is non-relativistic. Eventually, at $M \sim 3M_{solar}$ the system becomes unstable and collapses to a black hole.

7.8 Bose Condensation

We introduced the partition function for bosons by writing $Z_\mu^{(i)} = \sum_{n_i=0}^{\infty} \exp(-\beta n_i(\epsilon_i - \mu)) = [1 - \exp(-\beta(\epsilon_i - \mu))]^{-1}$. The condition of convergence for the sum is $\beta(\epsilon_i - \mu) > 0$, which is the most stringent for the lowest energy level: $\mu < 0$. We have seen that μ grows with decreasing T , but now we say it is limited to be less than zero. We can easily calculate n if $\mu = 0$. Let us denote it as n^* .

Let us start with the usual expression $N = \int_0^\infty \nu(\epsilon) n_{BE}(\epsilon) d\epsilon = C_1 V \int_0^\infty \sqrt{\epsilon} \frac{1}{e^{\beta\epsilon} - 1} d\epsilon$. The integral converges, giving $n^* \propto (kT)^{3/2}$. (For $\epsilon \ll kT$, the integrand $\propto kT/\sqrt{\epsilon}$.) Gathering all the constants, we get $n^* = \frac{2\Gamma(3/2)\zeta(3/2)}{\sqrt{\pi}} \lambda_T^{-3} = \zeta(3/2) \sqrt{\pi} \lambda_T^{-3} \approx 2.6 \lambda_T^{-3}$.

Here, $\zeta(s) = \frac{1}{\Gamma(s)} \int_0^{\infty} \frac{x^{s-1}}{e^x - 1} dx$ is Riemann zeta function.

We find a confusing result that the n^* decays as $T^{3/2}$. This is the maximal density at this temperature; a finite (negative) μ would only make n smaller. At some critical temperature T_C , such that $n^*(T_C) = n$, this “maximal” density will be reached. At lower temperatures, we apparently cannot accommodate the existing particles within n^* . Where do they go?

Let us look at $\sum_{p_x, p_y, p_z} = \int_0^{\infty} \nu(\epsilon) d\epsilon$. The original sum contains the lowest energy state with $\epsilon = 0$, while $\nu \propto \sqrt{\epsilon}$ gives it zero weight. This is not a good approximation when $\mu \rightarrow 0$. Let us add this state manually to the RHS: $N = C_1 V \int_0^{\infty} \sqrt{\epsilon} \frac{1}{e^{\beta\epsilon} - 1} d\epsilon + \frac{1}{e^{-\beta\mu} - 1} \approx N^*(T) + \frac{kT}{-\mu}$. Below T_C , a macroscopic number of particles $N - N^*(T)$ will reside on the lowest energy level – the “condensate”. The rest of them, $N^*(T)$ will be in the excited states “above the condensate”.

Below T_C , the chemical potential will be $\mu \approx \frac{-kT}{N - N^*(T)}$. This expression is $\sim N$ times smaller than the typical $\mu \sim -kT \ln(\dots)$ in the classical case. In fact, it is also smaller than the energy spacing between the energy levels, which explains why we singled out only the lowest level and not several of them.

7.9 Blackbody radiation

Consider a photon gas in equilibrium with a perfectly absorbing and emitting cavity. Photons are quanta of oscillations of electromagnetic waves, and similar to an example of a harmonic oscillator in Sec. 6.3 in these notes, the average number in a given mode (in a given oscillator) is $\frac{1}{e^{\beta\hbar\omega} - 1}$. We see that this expression corresponds to the BE-distribution with $\mu = 0$.

Let us calculate the energy in the photon gas: $U = \int_0^{\infty} \nu(\epsilon) \frac{1}{e^{\beta\epsilon} - 1} \epsilon d\epsilon$, where $\epsilon = \hbar\omega$. We purposefully neglect the zero-point energy $\hbar\omega/2$, which would give a divergent result. To calculate the density of states, we write the momentum of a photon as $p = \hbar\omega/c$. $\sum_{p_x, p_y, p_z} =$

$$V/h^3 \iiint_{-\infty}^{+\infty} d^3p = V/h^3 \int_0^{+\infty} 4\pi p^2 dp = \frac{V}{c^3 h^3} \int_0^{+\infty} 4\pi \epsilon^2 d\epsilon.$$

Since photons have 2 polarizations, this result should be multiplied by 2. Therefore, $\nu = \frac{8\pi\epsilon^2 V}{c^3 h^3}$ and $U = \int_0^{\infty} \frac{\epsilon^3 V}{\pi^2 c^3 h^3} \frac{1}{e^{\beta\epsilon} - 1} d\epsilon$.

It is instructive to rewrite this as a function of ω : $U = \int_0^\infty \frac{\hbar\omega^3 V}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} d\omega$ and look into the energy density per range of frequencies: $u_\omega = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$ (Planck's law). In the limit of high temperatures, $\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \approx kT$ (according to the equipartition theorem, the energy of an oscillator is kT) and we get a classical result $u_\omega \approx \frac{\omega^2 kT}{\pi^2 c^3}$ (Rayleigh-Jeans law, notice that \hbar does not enter). Integrated over all frequencies, this result diverges as $U \propto \int_0^\infty \omega^2 d\omega$. Planck's law fixes the problem, by introducing a high frequency cut-off, $\hbar\omega \sim kT$.

Going back to the full expression, the energy density per volume $u = \int_0^\infty \frac{\epsilon^3}{\pi^2 c^3 \hbar^3} \frac{1}{e^{\beta\epsilon} - 1} d\epsilon = \frac{(kT)^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$. The integral is $\pi^4/15$, and $u = \frac{\pi^2 (kT)^4}{15 c^3 \hbar^3}$.

To evaluate intensity, we imagine container with an opening of area A , through which the radiation is escaping. In time t , light propagates distance ct , and the escaping photons moving at an angle θ to the normal to the opening will be coming from a volume $ctA \cos(\theta)$. The energy emitted into an infinitesimal solid angle $d\Omega = 2\pi \sin(\theta) d\theta$ is $ctAu \cos(\theta) d\Omega/4\pi$. Integrating over θ from 0 to $\pi/2$ ($\theta < \pi/2$ for photons leaving the container), we get $\frac{ctAu}{2} \int_0^{\pi/2} \cos(\theta) \sin(\theta) d\theta = ctAu/4$. The intensity of radiation is this energy per unit time and area $cA/4 = \frac{\pi^2 (kT)^4}{60 c^2 \hbar^3}$ – Stefan-Boltzmann law.

Similarly, we could calculate the pressure. Here, instead of energy ϵ , each photon arriving at the wall transfers perpendicular momentum $2\epsilon/c \cos(\theta)$ (2 for reflection). Correspondingly, $P = \frac{2cu}{2c} \int_0^{\pi/2} \cos^2(\theta) \sin(\theta) d\theta = u/3$. This result is in fact more general, and $U = 3PV$ for any relativistic gas (both bosons and fermions) without internal structure. Indeed, similar to section 7.4 above, $PV = -\Omega = kT \ln Z_\mu = kT \ln \prod_i Z_\mu^{(i)} = kT \sum_i \ln Z_\mu^i = \pm kT \sum_i \ln[1 \pm e^{-\beta(\epsilon_i - \mu)}] = \pm kT \int \nu(\epsilon) \ln[1 \pm e^{-\beta(\epsilon - \mu)}] d\epsilon$. Taking $\nu(\epsilon) = C_2 V \epsilon^2$ for a relativistic gas, and integrating by parts, we get:

$$PV = \pm kTC_2 V \int \epsilon^2 \ln[1 \pm e^{-\beta(\epsilon - \mu)}] d\epsilon = \pm kTC_2 V \int \frac{1}{3} \epsilon^3 \frac{\pm \beta e^{-\beta(\epsilon - \mu)}}{1 \pm e^{-\beta(\epsilon - \mu)}} d\epsilon = \frac{1}{3} \int \nu(\epsilon) \epsilon \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1} d\epsilon = \frac{1}{3} U$$

7.10 Debay model

Dispersion: $\omega = sq$. DOS: $\nu = \frac{\epsilon^2}{2\pi^2 s^3 \hbar^3}$. Sum of $1/s_i^2$ over the three polarizations is replaced by $3/s^2$. Then $C_V = kV \int_0^{\hbar\omega_{max}} \frac{3\epsilon^2}{2\pi^2 s^3 \hbar^3} \frac{\epsilon^2}{2kT} \sinh^{-2} \frac{\epsilon}{kT} d\epsilon$, where $\omega_{max} \sim s/a$. The exact coefficient comes from counting the total number of modes to be the same as the number of the degrees of freedom, and is important only at high temperature to ensure that $C_V = 3Nk$. In the low temperature limit, $kT \ll \hbar\omega_{max}$, we could replace the upper limit of the integral by ∞ . Using $\int_0^{\infty} x^4 \sinh^{-2}(x/2) dx = (2\pi)^4/15$, we get

$$C_V = \frac{2\pi^2}{5} V k \left(\frac{kT}{\hbar s} \right)^3 = \frac{12\pi^4}{5} N k \left(\frac{T}{T_D} \right)^3$$

8 Second order phase transitions

8.1 Landau theory

Assume $G(T, M) = G_0(T) + A(T)M^2 + B(T)M^4$, where M is an *order parameter*, such as magnetization. There are only even terms in the expansion, because the energy of the system does not depend on the direction of magnetization, and G is assumed to be analytic, so no $|M|$ terms are allowed. Assume $B > 0$, otherwise a minimum of G would tend to infinity. For $A > 0$, $\min G$ is at $M = 0$, for $A < 0$, $\min G$ is at $M \neq 0$. Hence there is a transition at $A = 0$. Take $A = a(T - T_C)$. We can take $B(T) \approx B(T_C) \equiv B$. Overall,

$$G(T, M) = G_0(T) + a(T - T_C)M^2 + BM^4$$

Solving $\frac{\partial G}{\partial M} = 0$ to find the value of M which minimizes G : For $T > T_C$, $M = 0$ and $G(T) = G_0(T)$. For $T < T_C$, $\frac{\partial G}{\partial M} = 2a(T - T_C)M + 4BM^3 = 0$; $M = 0$ now corresponds to a maximum, and the minimum value of G corresponds to $M = \pm \sqrt{a(T - T_C)/2B}$. Plot, Curie temperature. Plugging in, $G(T) = G_0(T) + A(T)M^2 + B(T)M^4 = G_0(T) - a^2(T - T_C)^2/4B$. Notice that the behavior of G is now non-analytic: there is a jump in the second derivative. Specifically, $S = -\frac{\partial G}{\partial T}$ (continuously) changes from S_0 to $S_0 - a^2(T_C - T)/2B$ below the transition. Heat capacity $C = T \frac{\partial S}{\partial T}$ jumps (down) by $a^2 T_c / 2B$.

8.2 Susceptibility to the external field

In external field, $G(T, M) = G_0(T) + A(T)M^2 + B(T)M^4 - MH$. To find the equilibrium M below the T_C , we again have to minimize G : $\frac{\partial G}{\partial M} = 2a(T - T_C)M + 4BM^3 - H = 0$. We will care about the “susceptibility”, $\chi = \frac{\partial M}{\partial H}$, which is a response of M to an infinitesimal H . Take $\frac{\partial}{\partial H}$ of the previous equation:

$$\frac{\partial M}{\partial H}(2a(T - T_C) + 12BM^2) = 1$$

Plugging in $M(H = 0)$, we get $\chi = \frac{1}{2a(T - T_C)}$ above T_C and $\chi = \frac{1}{4a(T_C - T)}$ below T_C . Again, we see a critical exponent (-1) , which is universal – it does not depend on the details of the system.

8.3 Ising model

$$H = -1/2 \sum_{\text{neighboring } i,j} J s_i s_j - h \sum_i s_i.$$

8.4 Limit $T \rightarrow 0$ vs. $N \rightarrow \infty$

We have seen that in the $N \rightarrow \infty$ limit, $F/N = -kT \ln(2 \cosh \beta J) = -kT \ln[e^{\beta J}(1 + e^{-2\beta J})] \approx -J - kT e^{-2\beta J}$. On the other hand, the full expression at finite N was $Z = \lambda_1^N + \lambda_2^N = (e^{\beta J} + e^{-\beta J})^N + (e^{\beta J} - e^{-\beta J})^N = e^{N\beta J}[(1 + e^{-2\beta J})^N + (1 - e^{-2\beta J})^N] \approx e^{N\beta J}(2 + N^2 e^{-4\beta J})$. (Here, the first order terms cancelled, and the second order terms were approximated as $N(N - 1) \approx N^2$.) Then $F/N \approx -J - kT N e^{-4\beta J}$.