PC2230

Thermodynamics and Statistical Mechanics

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1 Introduction

There are generally two points of view to the world. They are the macroscopic and the microscopic. Examples of macroscopic variables are mass and temperature, while examples of microscopic variables are velocity and energy.

A thermodynamic system is an amount of matter confined by walls apart from its surroundings.

Definition 1.1 (Closed and isolated systems)**.** An isolated system is one that does not interact in any way with its surroundings. Both energy and matter is conserved.

A closed system is one that can only exchange energy with its surroundings. Only energy is conserved.

An open system is one that can exchange both energy and matter with its surroundings. Neither energy nor matter is conserved. □

2 Zeroth and first laws of thermodynamics

2.1 Zeroth law

The zeroth law states that thermal equilibrium is a transitive relation. Temperature, as we will see, is then the metaphysical thing that is equal for two objects in thermal equilibrium. It is also the measure of the tendency of an object to spontaneously give up energy to its surroundings.

2.2 Ideal gas law

The ideal gas law is given by

$$PV = Nk_BT.$$

Consider a piston that moves along the x-axis with some gas trapped behind it in a cylinder. We assume that the particles have no volume, and are non-interacting. The average pressure

felt by the piston due to a single molecule is given by

$$\begin{aligned} P &= \frac{\overline{F}_{x,\text{piston}}}{A} \\ &= -\left(\frac{-m\overline{v}_x^2}{L}\right)/A \\ &= \frac{m\overline{v}_x^2}{V} \end{aligned}$$

The second step comes from the fact that $\Delta v_n = -2v_x$ (elastic collisions) and $\Delta t = \frac{2L}{v_x}$ and using $F = m\frac{\Delta v}{\Delta t}$.

For N molecules, we have

$$\begin{aligned} \overline{P}V &= Nm\overline{v}_x^2 = Nk_BT \\ \frac{1}{2}m\overline{v}_x^2 &= \frac{1}{2}k_BT. \end{aligned}$$

At room temperature, $k_BT \approx \frac{1}{40}$eV, which is quite small. This is the average translational kinetic energy along x of the particles. In all 3 dimensions, the average kinetic energy is given by

$$\begin{aligned} \overline{K} &= \frac{1}{2}m(\overline{v}_x^2 + \overline{v}_y^2 + \overline{v}_z^2) = \frac{1}{2}m\overline{v}^2 = \frac{3}{2}K_BT \\ \overline{v}^2 &= \frac{3k_BT}{m} \end{aligned}$$

2.3 Equipartition theorem

We have previously derived

$$\frac{1}{2}m\overline{v}_x^2 = \frac{1}{k_B}T.$$

In fact, we can show (later on) that the energy of every quadratic degree of freedom it is equivalent to $\frac{1}{2}k_BT$. In general, the internal energy of a particle is given by

$$U = \frac{1}{2}k_BTfN$$

where f is the number of quadratic degrees of freedom per particle, and N is the number of particles. Examples of quadratic degrees of freedom are like kinetic energy $\frac{1}{2}mv_x^2$, rotational energy $\frac{1}{2}I\omega_x^2$, and elastic potential energy $\frac{1}{2}kx^2$.

2.4 Work

Work refers to the non-spontaneous transfer of energy into another system. Contrast this with heat, which is spontaneously transferred. We denote dW as the differential of work done on the system. We assume that the process is quasi-static, meaning it is so slow that thermal equilibrium is maintained through the process.

Example 2.1 (Piston)**.** This is also known as the general hydrostatic system.

$$\begin{aligned} \mathrm{d}W &= \vec{F} \cdot \mathrm{d}\vec{r} \\ &= F\,\mathrm{d}x \\ &= PA\,\mathrm{d}x \\ &= -P\,\mathrm{d}V\,. \end{aligned}$$

The volume decreases as the piston moves. Positive work is done on the piston when it is compressed. ◊

Example 2.2 (Wire)**.**

$$\mathrm{d}W = \vec{F} \cdot \mathrm{d}\vec{r} = F\,\mathrm{d}l\,.$$

◊

Example 2.3 (Surface)**.** A wire pulls a surface (perhaps a film of soap) that is L wide and S long. The wire is pulling along S, which is also the x axis.

$$\mathrm{d}W = \vec{F} \cdot \mathrm{d}\vec{r} = S \cdot L\,\mathrm{d}x = SL\frac{dA}{L} = S\,\mathrm{d}A\,.$$

◊

Example 2.4 (Electrochemical cell)**.** Consider a cell made up of two electrodes with a potential difference V. If the external potential of the cell is greater than the emf of the cell V, then a charge $\mathrm{d}Q$ flows through the circuit from the negative to positive electrode. Positive work is done on the cell by charging it.

$$\mathrm{d}W = VdQ.$$

◊

Example 2.5 (Dielectrics)**.** Consider two parallel plates of area A separated from each other by a length l. The potential difference between them is V. To increase the charge by $\mathrm{d}Q$ on the capacitor plates,

$$\mathrm{d}W = V\mathrm{d}Q = E \cdot l\mathrm{d}Q.$$

Now we place a dielectric of polarisation $\mathbf{P}$ between the plates. The electric displacement field $\mathbf{D}$ is given by $\mathbf{D} = \epsilon_0\mathbf{E} + \frac{\mathbf{P}}{Al}$. From Maxwell's equations we know

$$\boldsymbol{\nabla} \cdot \mathbf{D} = q_{\text{free}}.$$

and so (after some calculation) $Q = DA$, The work done by the battery is

$$\mathrm{d}W = ElA\mathrm{d}D = EV\,\mathrm{d}D = \epsilon_0 EV\,\mathrm{d}E + E\,\mathrm{d}P\,.$$

The first term is the work done to increase the electric field, and the second is the work done on the dielectric to polarize it. ◊

Example 2.6 (Paramagnetic systems)**.** Consider a paramagnetic toroid of cross sectional area A And length L with a coil of wire around it. When the current changes, an emf is induced given by

$$V = -NA\frac{\mathrm{d}B}{\mathrm{d}t}.$$

To maintain this current, the work done by the battery is

$$\begin{aligned} \mathrm{d}W &= -V\,\mathrm{d}Q \\ &= NA\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}B \\ &= NAI\mathrm{d}B. \end{aligned}$$

From Maxwell's equations we have

$$\oint H \cdot \mathrm{d}l = I_{\text{free}}.$$

So we have $HL = NI$. Together with $B = \mu_0 H + \mu_0 \frac{M}{AL}$,

$$\mathrm{d}W = HV\mathrm{d}B = HV\mu_o\mathrm{d}H + H\mu_0\mathrm{d}M.$$

The first term is the work done to increase the magnetic field, and the second is the work done on the paramagnetic system itself. $\Diamond$

Actually, work is not a state function since generally it depends on the path taken. Hence perhaps a more accurate notation would be δW and not $\mathrm{d}W$. In any case it does not really matter too much for us.

2.5 First law of thermodynamics

Conservation of energy gives us

$$\Delta U = Q + W$$

where ΔU is the change in internal energy, Q is the heat added *to* the system, and W is the work done *on* the system. Internal energy is a state function, and we can write its exact differential (even though it is the sum of two inexact differentials)

$$\mathrm{d}U = \delta Q + \delta W\,.$$

For reversible processes, intuition tells us that reversing the process is just the original but with signs swapped:

$$W \to -W \qquad Q \to -Q \qquad \Delta U \to -\Delta U.$$

2.6 Response functions

Experimentally it might be easier to measure the response of a system to some stimulus. For example, we have expansivity α, which is the change in volume with respect to temperature:

$$\alpha_y = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_y$$

A similar function is compressibility κ, the change in volume with respect to an applied force,

$$\kappa_y = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_y$$

Another common function is heat capacity C, which is the amount of heat needed to raise temperature,

$$C_y = \frac{Q}{\Delta T}.$$

Specific heat capacity is heat capacity per unit mass, $c = \frac{C}{m}$.

We might note that we can hold different variables constant while measuring these response functions. Take a piston filled with gas for example. In measuring the heat capacity of the gas, we can either hold the volume constant (by fixing the piston in place), or we can hold the pressure constant (by allowing the piston to move freely). In general we will get two different results.

Example 2.7. Take the piston filled with gas mentioned previously. Assume it is filled with an ideal gas. Then,

$$\begin{aligned} \mathrm{d}U &= \delta Q + \delta W = \delta Q - P\,\mathrm{d}V \\ \implies \delta Q &= \mathrm{d}U + P\,\mathrm{d}V\,. \end{aligned}$$

We can write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V\,.$$

Note that since out of the variables P, T, V, only 2 of them can be independent at any time so in write $\mathrm{d}U$ we have chosen to drop the $\mathrm{d}P$ term. Now substituting,

$$\begin{aligned} \delta Q &= \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + P\,\mathrm{d}V \\ \frac{\partial Q}{\partial T} &= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\frac{\mathrm{d}V}{\mathrm{d}T}. \end{aligned}$$

Therefore,

$$\begin{aligned} C_V &= \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \\ C_P &= \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P. \end{aligned}$$

Note that since U depends on T and V, and P also depends on T and V, $\left(\frac{\partial U}{\partial T}\right)_{V,P} = \left(\frac{\partial U}{\partial T}\right)_V$. $\Diamond$

2.7 Quasi static processes

We hold many things constant, below is a table of vocabulary and what they refer to

Held constant	Name
P	Isobaric
V	Isochoric
T	Isothermal
Q = 0	Adiabatic

Example 2.8. Say we compress an ideal gas adiabatically. So from the first law of thermodynamics,

$$\Delta U = W \qquad \mathrm{d}U = \delta W$$

From the equipartition theorem we understand that $W = NK_BT\frac{f}{2}$ where f is the number of quadratic degrees of freedom. So

$$\mathrm{d}U = NK_B\frac{f}{2}\,\mathrm{d}T\,.$$

Using the fact that $\delta W = -P\,\mathrm{d}V$,

$$\begin{aligned}
Nk_B\frac{f}{2}\,\mathrm{d}T &= -P\,\mathrm{d}V = -\frac{Nk_BT}{V}\,\mathrm{d}V \\
\frac{f}{2T}\,\mathrm{d}T &= -\frac{1}{V}\,\mathrm{d}V \\
\frac{f}{2}\int_{T_i}^{T_f}\frac{1}{T}\,\mathrm{d}T &= -\int_{V_i}^{V_f}\frac{1}{V}\,\mathrm{d}V \\
\frac{f}{2}\ln\frac{T_f}{T_i} &= -\ln\frac{V_f}{V_i} \\
\implies V_fT_f^{\frac{f}{2}} &= V_iT_i^{\frac{f}{2}}.
\end{aligned}$$

$\Diamond$

3 The Microcanonical ensemble and the second law

The fundamental principle of statistical physics is that all possible states will occur with equal probability.

There are two manifestations of this principle. The first comes if we have many configurations of the same system at a given point in time, and this forms an *ensemble*. The second comes from having copies of the same system (at equilibrium) over different points of time, and this forms an ensemble as well.

The first and second manifestations are not equal to each other. They are only the same if the system is able to visit all possible states over a long enough period of time (ergodic). If the system is not ergodic, statistical physics only applies to the first case. For us we will concern ourselves with ergodic systems only so we do not have to worry about this.

3.1 Microcanonical ensemble

A microcanonical ensemble is an ensemble formed by isolated systems. Recall that an isolated system does not exchange energy or particle number with its environment. We also have $E = U = \langle E\rangle$.

In the microcanonical ensemble the entropy is important, and this depends on the number of microstates Ω. From the entropy we can then relate to other variables like temperature. But first we have to know how to count microstates.

3.1.1 Counting discrete microstates

For a discrete system, say a collection of three coins, the configuration heads-heads-tail is a microstate. The configuration tail-tail-tail is another microstate. On the other hand, a *macrostate* is for example "three heads". We denote Ω as the number of microstates in a macrostate. So $\Omega(\text{three heads}) = 1$.

In general, coin flips and other two-level systems follows the binomial distribution with probability h of getting heads and t of getting tails:

$$\Pr[H \text{ heads in } N \text{ flips}] = \frac{\Omega(H \text{ heads})}{\Omega(\text{all})} = h^H t^{N-H} \frac{N!}{H!(N-H)!}$$

An useful fact is that if N is large enough, we may apply the central limit theorem and approximate the distribution with a Gaussian. From the above, we can apply a few tricks:

$$\begin{aligned}
\Pr[H \text{ heads in } N \text{ flips}] &= \exp[\ln(\Pr(H \text{ heads in } N \text{ flips}))] \\
\ln(\Pr(H \text{ heads in } N \text{ flips})) &= \ln\left(h^H t^{N-H} \frac{N!}{H!(N-H)!}\right) \\
&= H \ln h + (N-H)\ln t + \ln N! - \ln H! - \ln(N-H)!
\end{aligned}$$

Using Stirling's approximation, which states $\ln(N!) \approx N \ln N - N + O(\ln N)$, we have

$$\begin{aligned}
&\Pr[H \text{ heads in } N \text{ flips}] \\
&\approx \exp[H \ln h + (N-H)\ln t + N \ln N - N - H \ln H + H - (N-H)\ln(N-H) + N - H] \\
&= \exp[H \ln h + (N-H)\ln t + N \ln N - H \ln H - (N-H)\ln(N-H)].
\end{aligned}$$

Let the term in the exponential be $f(H)$. We may perform a Taylor expansion of $f(H)$ about its mean, which is at hN,

$$f(H) = f(\overline{H}) + f'(\overline{H})(H - \overline{H}) + \frac{1}{2!} f''(\overline{H})(H - \overline{H})^2 \cdots$$

The derivatives are found through ordinary means,

$$\begin{aligned}
f'(H) &= \ln h - \ln t - \ln H + \ln(N-H) \\
f''(H) &= -\frac{1}{H} - \frac{1}{N-H}.
\end{aligned}$$

Substituting in $\overline{H} = hN$, we find that actually $f'(\overline{H}) = 0$ and that $f''(\overline{H}) = -\frac{1}{Nth}$. Substituting this back into the exponential,

$$\begin{aligned}
&\Pr[H \text{ heads in } N \text{ flips}] \approx \exp\left(f(\overline{H}) - \frac{1}{2}\frac{1}{Nth}(H - \overline{H})^2\right) \\
&= A \exp\left[-\frac{(H-\overline{H})^2}{2Nth}\right].
\end{aligned}$$

This is a Gaussian with mean $\overline{H}$ and standard deviation $\sigma = \sqrt{Nth}$. Now normalization tells us that $A = \frac{1}{\sqrt{2\pi\sigma^2}}$.

3.1.2 Counting microstates for classical systems

Generally for classical systems we will be working with variables of momentum p and position x. The probability density function associated with these variables is simply given by

$$\Pr(\{p, r\} = \frac{1}{\Omega}$$

as long as the energy of the system (given by the Hamiltonian $\hat{H}$) lies within the energy range of the microcanonical emsemble, $E < \hat{H}(\{p, r\}) < E + \mathrm{d}E$.

In this case Ω also has a special name, the *phase space*. It is what we get when we consider all configurations, which is also a function of energy E, volume V and particle number N:

$$\int\limits_{E<\hat{H}<E+\mathrm{d}E} \{\mathrm{d}p, \mathrm{d}r\} = \Omega(E, V, N)$$

There are a few quantities related to Ω. The first is the cumulative volume in phase space,

$$\Phi(E, V, N) = \int\limits_{\hat{H}<E} \{\mathrm{d}p, \mathrm{d}r\}$$

If we think of the phase space as a 3D space, then Ω would be a shell of constant E, and Φ would be the space enclosed by the shell.

Next we also have the density of state

$$\omega(E, V, N) = \frac{\partial \Phi}{\partial E},$$

and is related to Ω through

$$\Omega(E, V, N) = \omega \cdot \Delta E.$$

To obtain the probability density for one variable, we have to integrate out all the other variables:

$$\Pr(r_1) = \int\limits_{r \neq r_1} \Pr(\{p_x, r\})\, \mathrm{d}p\, \mathrm{d}r = \frac{1}{\Omega} \int\limits_{r \neq r_1} \mathrm{d}p\, \mathrm{d}r$$

For example, for a single particle that can move in a single dimension,

$$\Pr(x) = \int_{-\infty}^{\infty} \Pr(x, p_x)\, \mathrm{d}p_x\,,$$

or for a single particle that can move in three dimensions,

$$\Pr(x) = \int_{-\infty}^{\infty} \Pr(x, p_x, y, p_y, z, p_z)\, \mathrm{d}p_x\, \mathrm{d}y\, \mathrm{d}p_y\, \mathrm{d}z\, \mathrm{d}p_z\,.$$

3.2 Maxwell-Boltzmann distribution

Suppose we have a box of volume V with dimensions $L_x \times L_y \times L_z$. Furthermore for the i-th molecule we have variables position r_i and momentum p_i associated with it. The Hamiltonian for a single particle is given by

$$\hat{H}(\{p, r\}) = \sum_{i=x,y,z} \frac{p_i^2}{2m}.$$

The aim is to find $\Pr(x)$ and $\Pr(p_x)$. Finding $p(x)$ is straightforward, it is simply $\frac{1}{L_x}$. Finding $\Pr(p_x)$ is slightly more work. We have to start from the basics and find $\Phi(E)$.

If we consider the energy of N particles, we have

$$E = \sum_{i}^{3N} \frac{p_i^2}{2m}$$

If we only have one particle then the p-phase space would be a sphere of radius $\sqrt{2mE}$. With N particles, then this would be a sphere in $3N$-dimensions but still with radius $\sqrt{2mE}$. The volume of an α-dimensional sphere is given by $V = \frac{\pi^{\frac{\alpha}{2}}}{(\frac{\alpha}{2})!} R^{\alpha}$. Thus,

$$\begin{aligned}
\Phi &= \int_{H<E} \{\mathrm{d}p, \mathrm{d}r\} \\
&= V_{box}^N \frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!} R^{3N} \\
&\vdots \\
&= \left[V^N \left(\frac{4\pi e m E^{\frac{3N}{2}}}{3N} \right) \right] \\
&\propto E^{\frac{3N}{2}}
\end{aligned}$$

where we have used Stirlings approximation to get $(\frac{3N}{2})! \approx \exp\left[\frac{3N}{2} \ln(\frac{3N}{2}) - \frac{3N}{2}\right] = (\frac{3N}{2e})^{\frac{3N}{2}}$.

Next, we need to determine $\omega = \frac{\partial \Phi}{\partial E}$. We use the trick that if $\Phi \propto E^{3N/2}$, then $\omega = \frac{\partial \Phi}{\partial E} = \frac{3N}{2} \frac{\Phi}{E}$.

Finally, we can find $\Omega = \omega \Delta = \frac{3N}{2} \frac{\Phi}{E} \Delta$. Since $\Pr(p_x) = \frac{\Omega_{p_x}}{\Omega}$, we want to find Ω_{p_x} as well. But Ω_{p_x} is precisely Ω but when the total energy is instead $E - \frac{p_x^2}{2m}$, and when the number of dimensions go from $3N$ to $3N-1$. Hence, with $\delta = \frac{p_x^2}{2m}$, we have

$$\begin{aligned}
\Omega_{p_x} &= \left(\frac{3N}{2E} \right) V^N \left(\frac{4\pi e m E)}{3N} \right)^{\frac{3N}{2}} \Delta \\
\Omega_{p_x} &= \left(\frac{3N-1}{2(E-\epsilon)} \right) V^N \left(\frac{4\pi e m (E-\epsilon)}{3N-1} \right)^{\frac{3N-1}{2}} \Delta
\end{aligned}$$

Now, putting it all together,

$$\begin{aligned}\Pr(p_x) &= \frac{\Omega(E - \frac{p_x^2}{2m}, V, N-1)}{\Omega(E, V, N)} \\ &= \frac{3N-1}{3N}\frac{E}{E-\epsilon}\left(\frac{4\pi e m}{3}\right)^{\frac{-1}{2}} \underbrace{\left(\frac{(N-1/3)^{-\frac{3N+1}{2}}}{N^{-\frac{3N}{2}}}\right)}_{A}\underbrace{\left(\frac{(E-\epsilon)^{\frac{3N-1}{2}}}{E^{\frac{3N}{2}}}\right)}_{B}\end{aligned}$$

TODO.

We get at last

$$\begin{aligned}\Pr(p_x) &= \frac{1}{\sqrt{4\pi m\langle\epsilon\rangle}}\exp\left(-\frac{\epsilon}{2\langle\epsilon\rangle}\right) \\ &= \frac{1}{\sqrt{2\pi\langle p_x^2\rangle}}\exp\left(-\frac{p_x^2}{2\langle p_x^2\rangle}\right).\end{aligned}$$

This is a Gaussian with mean 0 and variance $\langle p_x^2\rangle$. Now according to the equipartition theorem, $\frac{\langle p_x^2\rangle}{2m} = \frac{1}{2}k_BT$, so re-expressing, we have

$$\Pr(p_x) = \frac{1}{\sqrt{2\pi m k_B T}}\exp\left(-\frac{p_x^2}{2mk_BT}\right).$$

The probability of finding a particle with momentum p_x is $\Pr(p_x)\,\mathrm{d}p_x = \Pr(v_x)\,\mathrm{d}v_x$. Hence, we also have

$$\begin{aligned}\Pr(v_x) &= \Pr(p_x)\frac{\mathrm{d}p_x}{\mathrm{d}v_x} \\ &= \sqrt{\frac{m}{2\pi m k_B T}}\exp\left(-\frac{mv_x^2}{2k_BT}\right).\end{aligned}$$

We can also express it in terms of speed, which perhaps looks more familiar:

$$\begin{aligned}\Pr(v)\,\mathrm{d}v &= \int \mathrm{d}\Omega\, v^2\,\mathrm{d}v\, p^3(v = v_x) \\ &= 4\pi v^2\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}}\exp\left(-\frac{mv^2}{2k_BT}\right).\end{aligned}$$

3.3 Entropy and temperature

Entropy S is defined as

$$S = k_B \ln\Omega$$

It has units J/K. S is also a state function. It is an extensive variable since in general it depends on the particle number.

Consider now two systems. The two systems are closed, so particles and energy cannot leave, but they can still interact with each other. We also assume that there is no work done between them, and that the microstates in both systems are independent of each other. Then temperature,

intuitively, is what we get when the two systems achieve equilibrium. When the system achieves equilibrium, then this is represented by the maximum of the probability density function $p(E)$. So we want to find when $\frac{\mathrm{d}p}{\mathrm{d}E} = 0$, when $p(E)$ is maximum.

$$p(E_1) = \frac{\Omega_{total}(E_1)}{\Omega_{total}(all)} = \frac{\Omega_1(E_1)\Omega_2(E_2)}{\Omega(E)} = \frac{\Omega_1(E_1)\Omega_2(E-E_1)}{\Omega(E)}$$

Since the function ln is monotone, if we can find the maximum for $\ln p$ then we would have found the maximum for p. So

$$\begin{aligned}
\ln p(E_1) &= \ln \frac{\Omega_1(E_1)\Omega_2(E-E_1)}{\Omega(E)} \\
&= \frac{1}{k_B}[S_1(E_1) + S_2(E-E_1) - S(E)] \\
\frac{\partial}{\partial E_1}(\ln p(E_1)) &= \frac{1}{k_B}\left[\frac{\partial}{\partial E_1}S_1(E_1) - \frac{\partial}{\partial E_2}S_2(E_2) - 0\right]
\end{aligned}$$

Hence at equilibrium the maximum is achieved when

$$\frac{\partial}{\partial E_1}S_1(E_1) = \frac{\partial}{\partial E_2}S_2(E_2)$$

Hence this expression gives us the *temperature* for each system. To maintain the consistency of units, this expression is actually equal to $\frac{1}{T}$, so

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{\delta W=0}$$

3.4 Second law of thermodynamics

Consider the same two isolated systems. Let the equilibrium energy of the first system be E_1'. So in equilibrium we have $E_1 = E_1'$. What happens if we are not in equilibrium? Then first of all $p(E_1) \leq p(E_1')$. This means that

$$\begin{aligned}
\frac{\Omega_1(E_1)\Omega_2(E-E_1)}{\Omega(E)} &\leq \frac{\Omega_1(E_1')\Omega_2(E-E_1')}{\Omega(E)} \\
1 &\leq \frac{\Omega_1(E_1')\Omega_2(E-E_1')}{\Omega_1(E_1)\Omega_2(E-E_1)} \\
k_B \ln 1 &\leq k_B \ln \Omega_1(E_1') + k_B \ln \Omega_2(E-E_1') - k_B \ln \Omega_1(E_1) - k_B \ln \Omega_2(E-E_1) \\
0 &= S_1(E_1') - S_1(E_1) + S_2(E_2') - S_2(E_2) \\
&= \Delta S_1 + \Delta S_2.
\end{aligned}$$

Therefore, we get the first statement of the second law,

$$\Delta S \geq 0.$$

Next, consider another system where the first system is immersed in a bath, but they are both still microcanonical. Being a bath means that T_2 does not change, though they can still exchange heat. Exchanging heat means that $\delta Q_2 = \delta Q_1$. Thus,

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial Q_2} \\ \mathrm{d}S_2 &= \frac{\delta Q_2}{T_2} = \frac{-\,\delta Q_1}{T_2}.\end{aligned}$$

We have previously shown that $\mathrm{d}S \geq 0$, so

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = \mathrm{d}S_1 - \frac{\delta Q_1}{T_2} \geq 0$$

so we get

$$\mathrm{d}S_1 \geq \frac{\delta Q_1}{T_2}.$$

Equality holds when the process is reversible.

From the first law, we know that

$$\mathrm{d}U \Big|_{\delta W = 0} = \delta Q.$$

From the second law, we also know that

$$\mathrm{d}U \Big|_{\delta W = 0} \leq T\,\mathrm{d}S\,.$$

With the addition of work,

$$\mathrm{d}U \leq T\,\mathrm{d}S + \delta W.$$

Quasi-static processes are reversible. If the process is reversible then the equality holds.

Example 3.1. Suppose we have some system where the work is expressed as $\delta W = -P\,\mathrm{d}V + \mu_0 H\ \mathrm{d}M + E\,\mathrm{d}P$. Then,

$$\begin{aligned}\mathrm{d}S &= \frac{1}{T}\,\mathrm{d}U + \frac{1}{T}P\,\mathrm{d}V - \frac{1}{T}\mu_0 H\ \mathrm{d}M - \frac{1}{T}E\,\mathrm{d}P \\ &= \left(\frac{\partial S}{\partial U}\right)_{V,M,P}\mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,M,P}\mathrm{d}V + \left(\frac{\partial S}{\partial M}\right)_{U,V,P}\mathrm{d}M + \left(\frac{\partial S}{\partial P}\right)_{U,V,M}\mathrm{d}P\end{aligned}$$

Note that we only hold the independent variables constant, which are those variables in the differentials. For example there is no $\left(\frac{\partial S}{\partial U}\right)_{P,H,E}\mathrm{d}U$ term. These partial derivatives give us an idea of how fast the entropy is changing with respect to the other variables. $\Diamond$

Example 3.2. Back to our ideal gas. The Maxwell-Boltzmann distribution gives

$$\Omega_{p_x} = \left(\frac{3N\Delta}{2U}\right)V^N\left(\frac{4\pi emE)}{3N}\right)^{\frac{3N}{2}}$$

From this we can find

$$\begin{aligned}S &= k_B \ln\Omega \\ &= k_B\left[\ln\frac{3N\Delta}{2U} + \ln V^N + \ln\left(\frac{4\pi emU}{3N}\right)^{\frac{3N}{2}}\right]\end{aligned}$$

Now S depends on U, V, N. Therefore,

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,V} \mathrm{d}N$$

First of all we have

$$\begin{aligned}
\frac{1}{T} &= \left(\frac{\partial S}{\partial U}\right)_{V,N} \\
&= k_B\left[-\frac{1}{U} + \frac{3N}{2U}\right] \\
U &= \left(\frac{3N}{2} - 1\right)k_B T.
\end{aligned}$$

This agrees with the equipartition theorem in the limit of large N. We also have

$$\begin{aligned}
\frac{P}{T} &= \left(\frac{\partial S}{\partial V}\right)_{U,N} \\
&= k_B\left(\frac{N}{V}\right) \\
PV &= Nk_B T.
\end{aligned}$$

$\Diamond$

Example 3.3. Consider an ensemble of N two-state systems. There are N_0 of them in state $|0\rangle$ and N_1 of them in $|1\rangle$. So $N = N_0 + N_1$, and $U = 0N_0 + EN_1 = EN_1$.

$$\Omega = \frac{N!}{N_1!N_0!}$$

Taking the limit $N_1 \to 0$, we have $\Omega \to 1$. The same occurs if we take the limit $N_1 \to N$. Also note that the maximum Ω occurs when $N_1 = \frac{N}{2}$. This then tells us that S is maximized at $N_1 = \frac{N}{2}$, and $S = 0$ at $N_1 = 0$ or $N_1 = N$.

Using Stirling's approximation,

$$\begin{aligned}
S &= k_B \ln \frac{N!}{N_1!N_0!} \\
&\approx k_B[N\ln N - N - N_1 \ln N_1 + N_1 - N_0 \ln N_0 + N_0] \\
S(N_1) &= k_B[N\ln N - N_1 \ln N_1 - (N - N_1)\ln(N - N_1)] \\
S(U) &= k_B\left[N\ln N - \frac{U}{E}\ln\frac{U}{E} - \left(N - \frac{U}{E}\right)\ln\left(N - \frac{U}{E}\right)\right]
\end{aligned}$$

What is odd about this system is that the entropy starts to decrease with increasing energy after a certain point. This means

$$\frac{1}{T} = \frac{\partial S}{\partial U} < 0$$

and so we end up with negative temperature. Let us evaluate it completely.

$$\begin{aligned}
\frac{1}{T} &= \frac{\partial S}{\partial N_1}\frac{\partial N_1}{\partial U} \\
&= k_B[-\ln N_1 + \ln(N - N_1)]\frac{1}{E} \\
\frac{E}{k_B T} &= \ln\left(\frac{N}{N_1} - 1\right) \\
N_1 &= \frac{N}{1 + \exp\left(\frac{E}{k_B T}\right)} \\
U &= \frac{EN}{1 + \exp\left(\frac{E}{k_B T}\right)}
\end{aligned}$$

Using this we can also find heat capacity,

$$\begin{aligned}
C_N &= \left(\frac{\partial U}{\partial T}\right)_N \\
&= N k_B \left(\frac{E^2}{k_B^2 T^2}\right) \frac{\exp\left(\frac{E}{k_B T}\right)}{\left[1 + \exp\left(\frac{E}{k_B T}\right)\right]^2}
\end{aligned}$$

As $T \to 0$, the exponential decay dominates, and we have $C_N \to 0$. When $T \to \infty$, we find that the exponential goes to 0, and so $C_N \sim \frac{1}{T^2}$. This illustrates the energy gap behaviour. The excited states are only going to be populated if the thermal energy starts to exceed the energy gap, or $k_B T > E$.

To find the probability of occupying an excited or ground state can be given by

$$p(n) = \frac{\Omega_n}{\Omega},$$

where $n = 0, 1$, representing the ground state or excited state. We can find Ω_n by finding Ω but when $N \to N - 1$ and $N_1 \to N_1 - n$. Therefore, we have

$$p(n) = \frac{\Omega(N - 1, N_1 - n)}{\Omega(N, N_1)}$$

$\Diamond$

4 Maxwell relations and energies

4.1 Maxwell relations

The Maxwell relations relate quantities that are hard to measure (such as entropy) to quantities that are easier to measure (such as temperature and volume). In this section we will derive these relations.

First consider the internal energy. Later on we will meet more types of energies and the way we know what to use is through the independent variables. For instance we have

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu_0 H\mathrm{d}M + \dots$$

The independent variables are the variables in the differentials. Furthermore, we usually see T and S go together in this way, and they are known as *canonical conjugate variables*. Similarly for the other pairs. We can also write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,M} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,M} \mathrm{d}V + \left(\frac{\partial U}{\partial M}\right)_{S,V} \mathrm{d}M\,,$$

which gives us

$$T = \frac{\partial U}{\partial S} \qquad P = -\frac{\partial U}{\partial V} \qquad \mu_0 H = \frac{\partial U}{\partial M}$$

and so on. We can actually relate any two of them with each other:

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S \\ &= \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V \\ &= -\left(\frac{\partial P}{\partial S}\right)_V\end{aligned}$$

This is one of the Maxwell relations.

Example 4.1. Consider a one-dimensional wire of length l under some tension F. We have

$$\mathrm{d}U = T\mathrm{d}S + F\mathrm{d}l.$$

Therefore

$$\begin{aligned}\left(\frac{\partial T}{\partial l}\right)_S &= \left[\frac{\partial}{\partial l}\left(\frac{\partial U}{\partial S}\right)_l\right]_S \\ &= \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial l}\right)_S\right]_l \\ &= \left(\frac{\partial F}{\partial S}\right)_l\end{aligned}$$

◊

Example 4.2. Let us apply the Maxwell relations to heat capacities. We have

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial Q}{\partial T}\right)_P.$$

Using the second law we know $\delta Q = T\mathrm{d}S$ so we can write

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

Now applying a partial derivative identity,

$$\begin{aligned}C_P &= T\left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] \\ &= C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P\end{aligned}$$

◊

4.1.1 Helmholtz free energy

The previous examples were micro canonical ensembles. Now let us consider a system immersed in a heat bath and $\delta Q \neq 0$. We can control all the other usual independent variables. Furthermore, we have traded over entropy for temperature since now entropy is no longer the independent variable but temperature is. Hence we will be considering another type of energy, the *Helmholtz free energy* F. It is defined as

$$F = U - TS$$

The second term is where the substitution of S for T occurs[1]. Let us evaluate the differential:

$$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= T\mathrm{d}S + \delta W - T\mathrm{d}S - S\mathrm{d}T \\ &= -S\mathrm{d}T + \delta W \\ &= -S\mathrm{d}T - P\mathrm{d}V + \mu_0 H\mathrm{d}M + \dots \end{aligned}$$

Of course then we can relate this to

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{V,M} \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_{T,M} \mathrm{d}V + \left(\frac{\partial F}{\partial M}\right)_{T,V} \mathrm{d}M$$

giving us

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,M} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,M} \qquad \mu_0 H = -\left(\frac{\partial F}{\partial M}\right)_{T,V}$$

Then one of the Maxwell relations is

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left[\frac{\partial}{\partial V}\left(-\frac{\partial F}{\partial T}\right)_V\right]_T \\ &= \left[\frac{\partial}{\partial T}\left(-\frac{\partial F}{\partial V}\right)_T\right]_V \\ &= \left(\frac{\partial P}{\partial T}\right)_V. \end{aligned}$$

4.1.2 Enthalpy

We still have a system similar to a micro canonical ensemble but we control S, P (instead of V), and N. From the previous section we know we should use the Helmholtz free energy

$$H = U - (-PV) = U + PV.$$

so

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S.$$

[1] This is kind of similar to the transformation from the Lagrangian to the Hamiltonian, where we have $\mathcal{H} = p\dot{q} - \mathcal{L}$.

4.1.3 Gibbs free energy

Here we have $U(S, V, N, M, \dots)$ as a function of the usual extensive variables. We get the Gibb's free energy of the system if we trade all of them for their canonical conjugates and leave only N to be controlled. So

$$G(T, P, N, H, \dots) = U - TS + PV - \mu_0 HM + \dots$$

and the differential is

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P - \mu_0 M\mathrm{d}H + \dots \mu\mathrm{d}N.$$

4.2 Observations

Deriving every single Maxwell relation can be tedious work. Let us look at a previously derived relation for the one dimensional wire.

$$\left(\frac{\partial T}{\partial l}\right)_S = \left(\frac{\partial F}{\partial S}\right)_l.$$

Note that (T, S) and (F, l) are conjugate variables and they appear at the same locations on both sides of the equation. The sign is determined by the form of energy we use in the derivation of the relation.

Example 4.3. Say we wish to relate $\frac{\partial S}{\partial M}$ to another variable. The canonical conjugate of S is T. So it would be something like

$$\left(\frac{\partial S}{\partial M}\right)_T = \pm\left(\frac{\partial ?}{\partial T}\right)_M$$

The canonical conjugate of M is $\mu_0 H$, so we have

$$\left(\frac{\partial S}{\partial M}\right)_T = \pm\mu_0\left(\frac{\partial H}{\partial T}\right)_M$$

We need to find an energy with term $\pm S\mathrm{d}T \pm \mu_0 H\mathrm{d}M$. The only one that satisfies this is the Helmholtz free energy $\mathrm{d}F = -S\mathrm{d}T + \mu_0 H\mathrm{d}M$. So in fact there is a need for a negative sign:

$$\left(\frac{\partial S}{\partial M}\right)_T = -\mu_0\left(\frac{\partial H}{\partial T}\right)_M$$

$\Diamond$

Example 4.4 (Application)**.** Given an elastic rod under tension $F = (a + bT)(l - l_0)$ and of heat capacity $C_l = \alpha T^3$, we wish to find the entropy $S(T, L)$.

First, since both F and S depends on T and l only, we can write

$$F = \left(\frac{\partial F}{\partial T}\right)_l \mathrm{d}T + \left(\frac{\partial F}{\partial l}\right)_T \mathrm{d}l$$
$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_l \mathrm{d}T + \left(\frac{\partial S}{\partial l}\right)_T \mathrm{d}l.$$

We know that $C_l = T\left(\frac{\partial S}{\partial T}\right)_l$. So we wish to find $\left(\frac{\partial S}{\partial l}\right)_T$. We can derive a Maxwell relation

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial F}{\partial T}\right)_l = b(l - l_0).$$

The negative sign again comes from the use of the Helmholtz free energy. Now we solve for the equation of state. First from $\left(\frac{\partial S}{\partial T}\right)_l = \alpha T^2$ we get

$$S = \frac{1}{3}\alpha T^3 + f(l).$$

this means

$$\left(\frac{\partial S}{\partial l}\right)_T = \frac{\partial f}{\partial l} = -b(l - l_0)$$

Thus

$$f = -\frac{b}{2}(l - l_0)^2 + C$$

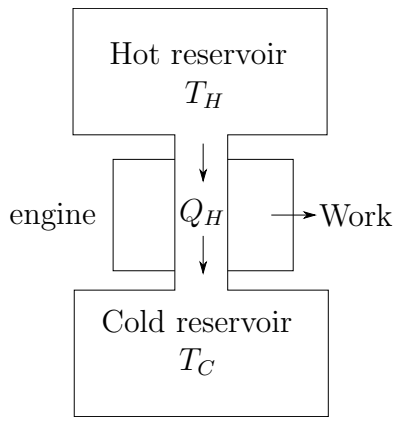
and so

$$S = \frac{1}{3}\alpha T^3 - \frac{b}{2}(l - l_0)^2 + C.$$

$\Diamond$

5 Heat engines

Heat engines are devices that can absorb heat from a hot reservoir and convert some of that thermal energy to work.



There are two large classes of heat engines, the external combustion engine (e.g. steam engine) and the internal combustion engine (e.g. gasoline engine). However in both cases they usually take both substances around a closed loop in the PV diagram. Since U is a state function, it does not depend on the path taken and so in a closed loop $\Delta U = 0$. This means

$$\oint \mathrm{d}U = 0 = \oint \delta Q - \oint P\mathrm{d}V.$$

If $\oint P\mathrm{d}V > 0$, the engine does work on its surroundings. Then to maintain $\oint \mathrm{d}U = 0$, we have $\oint T\mathrm{d}S > 0$, i.e. heat is added to the system.

One of our goals will be to find the efficiency η of a heat engine. Efficiency is defined as

$$\eta = \frac{W_{out}}{|Q_H|}.$$

From the above we find $W_{out} = \oint P\mathrm{d}V = \oint T\mathrm{d}S = |Q_H| - |Q_C|$. Therefore generally $\eta = 1 - \frac{|Q_C|}{|Q_H|}$.

5.1 Carnot cycle

The Carnot cycle is carried out by any substance that undergoes only isothermal and adiabatic changes.

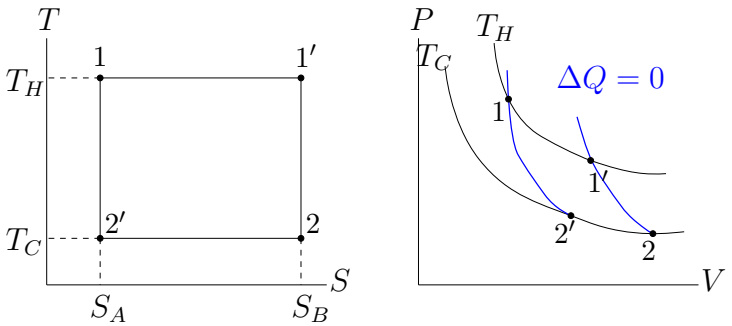


Figure 1: $1 \to 1'$ Isothermal expansion. $1' \to 2$ Adiabatic expansion. $2 \to 2'$ Isothermal compression. $2' \to 1$ Adiabatic compression.

Let us figure out its efficiency.

$$\begin{aligned} W_{out} &= \oint P\mathrm{d}V \\ &= \oint T\mathrm{d}S \\ &= (T_H - T_C)(S_B - S_A) \end{aligned}$$

The heat was added between 1 and $1'$ so

$$\begin{aligned} Q_H &= \int_1^{1'} T\mathrm{d}S \\ &= T_H(S_B - S_A) \end{aligned}$$

Therefore

$$\eta = 1 - \frac{T_C}{T_H}.$$

This looks like the general formula for η we derived above. However due to the second law of thermodynamics $\delta Q \leq T\mathrm{d}S$ this is actually more efficient and is known as *Carnot's bound* on the efficiency of heat engines.

5.2 Stirling cycle

Below we illustrate a Stirling engine. The crankshaft keeps the cylinder and piston at a 90° phase angle.

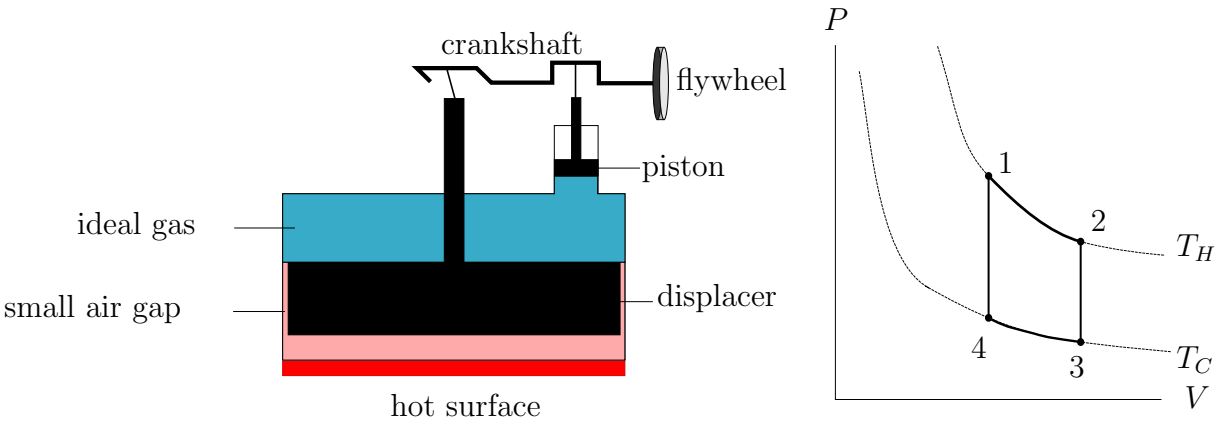


Figure 2: $1 \to 2$ isothermal expansion. $2 \to 3$ isochoric cooling. $3 \to 4$ isothermal contraction. $4 \to 1$ isochoric heating.

Let us calculate the heat transferred. For $1 \to 2$, we have $\delta Q = -\delta W$ and so

$$Q_{12} = -W_{12} = \int_1^2 \frac{Nk_B T_H}{V} \mathrm{d}V = Nk_B T_H \ln \frac{V_2}{V_1}.$$

For $2 \to 3$, we can express it in terms of the heat capacity,

$$Q_{23} = C_V(T_C - T_H).$$

For $3 \to 4$ is the reverse of $1 \to 2$,

$$Q_{34} = Nk_B T_C \ln \frac{V_4}{V_3} = Nk_B T_C \ln \frac{V_1}{V_2}.$$

Similarly for $4 \to 1$

$$Q_{41} = C_V(T_H - T_C) = -Q_{23}$$

The work done by the engine is thus

$$\begin{aligned} W_{out} &= Q_{12} + Q_{34} \\ &= Nk_B(T_H - T_C) \ln \frac{V_2}{V_1} \end{aligned}$$

and so the efficiency is

$$\eta = \frac{Nk_B(T_H - T_C) \ln \frac{V_2}{V_1}}{Nk_B T_H \ln \frac{V_2}{V_1} + C_V(T_H - T_C)}$$

The displacer also acts as a regenerator. It stores heat to be used in the next cycle. Thus in the limit of a perfect regenerator, we have

$$\begin{aligned} \eta &= \frac{Nk_B(T_H - T_C) \ln \frac{V_2}{V_1}}{Nk_B T_H \ln \frac{V_2}{V_1}} \\ &= 1 - \frac{T_C}{T_H} \end{aligned}$$

which is the same as Carnot's bound.

5.3 Refrigerator

A refrigerator it is the reverse of a heat engine. We put in work to move heat from a cold reservoir to a hot reservoir instead.

5.4 Third law of thermodynamics

The third law states that at $T = 0$ the entropy of a substance is independent of other variables (becomes a constant). It is a result of quantum mechanics, the idea behind it being that at $T = 0$, the number of states Ω is just the number of ground state the system has.

Example 5.1. Consider a hydrostatic system with thermal expansion

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P.$$

We wish to find the behaviour of α as $T \to 0$. We want to relate $\left(\frac{\partial V}{\partial T}\right)_Q$ with something else. It can only be $\left(\frac{\partial S}{\partial P}\right)_T$. Therefore since we have the Gibb's free energy as

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P,$$

this gives us

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

and so we see that $\alpha \to 0$ due to the third law. $\Diamond$

6 Canonical ensemble

6.1 Derivation of the canonical ensemble

In a microcanonical ensemble, we consider an isolated system where energy E and number of particles N were fixed. Most of the thermodynamic variables were found through relation to entropy S. For large systems, the canonical ensemble is an easier way of calculating these variables.

In a canonical ensemble, we consider a closed system where instead of controlling E, we control temperature T instead. N is still held fixed. So we can exchange energy with a thermal bath, but not particle numbers.

Let the system we are interested in be called A and the bath be called B. Heat can be exchanged between them. The probability for the system to be in a given state x from the microcanonical ensemble is given by

$$\Pr(x) = \frac{\Omega(x)}{\Omega_{\text{all}}}$$

If A is described by continuous variables, say momentum p and position q,

$$\Pr(\{p_A, q_A\}) = \frac{\Omega_A(\{p_A, q_A\})\Omega_B(\text{consistent with } \{p_a, q_A\})}{\Omega_{all}}$$

In terms of energies, since the total energy E is fixed,

$$\Pr(\{p_A, q_A\}) = \frac{\Omega_A(\{p_A, q_A\})\Omega_B(E_B)}{\Omega(E)}$$

In terms of entropies,

$$\begin{aligned} k_B \ln \Pr(\{p_A, q_A\}) &= k_b \ln \Omega_A(\{p_A, q_A\}) + k_B \ln \Omega_B(E_B) - k_B \ln \Omega(E) \\ &= S_A + S_B(E - E_A) - S(E) \end{aligned}$$

Since A is in a given state, there is only one single configuration for A, and so $\Omega_A = 1$ and $S_A = 0$. For the second term, we do a Taylor expansion about E (since most of the energy comes from the bath)

$$S_B(E - E_A) \approx S_B(E) - \frac{\partial S_B(E)}{\partial E} E_A$$

Substituting,

$$\begin{aligned} k_B \ln \Pr(\{p_n, q_n\}) &= S_B(E) - \frac{\partial S_B(E)}{\partial E} E_A - S(E) \\ &= -\frac{1}{T}\mathscr{H}_A(\{p_A, q_A\}) + S_B(E) - S(E) \end{aligned}$$

where $\mathscr{H}$ is the Hamiltonian. Inverting the expressions,

$$\Pr(\{p_n, q_n\}) = \exp\left[-\frac{1}{k_B T}\mathscr{H}_A(\{p_A, q_A\})\right] \exp\left[\frac{s_B(E) - S(E)}{k_B}\right]$$

We note that the second exponential is constant with respect to system A. Therefore,

$$\Pr(\{p, q\}) \propto \exp\left[-\frac{1}{k_B T}\mathscr{H}(\{p, q\})\right]$$

Probabilities have to be normalised,

$$\int \Pr(\{p, q\}) \mathrm{d}p_1 \cdots \mathrm{d}p_n \mathrm{d}q_1 \cdots \mathrm{d}q_m = 1$$

where n is N times the number of degrees of freedom per particle. Actually, for the units to match, since $[p \times q] = [h]$, or J s, so we should write

$$\left(\frac{1}{h}\right)^n \int \Pr(\{p, q\}) \mathrm{d}p_1 \cdots \mathrm{d}p_n \mathrm{d}q_1 \cdots \mathrm{d}q_n = 1$$

The reciprocal of this gives us the normalisation constant. To write it out in full we have

$$\Pr(\{p, q\}) = \frac{\exp\left(-\frac{1}{k_B T}\mathscr{H}(\{p, q\})\right)}{\frac{1}{h^n}\int \exp\left(-\frac{1}{k_B T}\mathscr{H}(\{p, q\})\right) \mathrm{d}\{p, q\}}$$

Now, assume that although A is small relative to B, it is still large enough for thermodynamics to apply. Then,

$$S(E) = S(U) = S_A(E_A) + S_B(E_B) = S_A(\langle E_A \rangle) + S_B(\langle E_B \rangle).$$

We can expand $S_B(E)$ about $\langle E_B \rangle$,

$$\begin{aligned} S_B(E) &\approx S_B(\langle E_B \rangle) + \frac{\partial S_B(E)}{\partial E} \\ &= S_B(\langle E_B \rangle) + \frac{1}{T}(E_A) \end{aligned}$$

This gives us

$$\begin{aligned} S_B(E) - S(E) &= S_B(E) - S_A(\langle E_A \rangle) - S_B(\langle E_B \rangle) \\ &= \frac{\langle E_A \rangle}{T} - S_A(\langle E_A \rangle) \\ k_B \ln \Pr(\{p_A, q_A\}) &= -\frac{\mathscr{H}(\{p_A, q_A\})}{T} + \frac{\langle E_A \rangle}{T} - S_A(\langle E_A \rangle) \end{aligned}$$

and inverting, we have

$$\Pr(\{p_A, q_A\}) = \frac{\exp\left(-\frac{\mathscr{H}(\{p_A, q_A\})}{k_B T}\right)}{\exp\left(-\frac{\langle E_A \rangle - TS_A}{k_B T}\right)}$$

So we get a nicer normalisation constant without the huge integral.

6.2 Partition functions

Another name for the normalisation is also called the *partition function*. For convenience, let $\beta = \frac{1}{k_B T}$. For continuous classical systems, as we have just seen,

$$Z_N = \int \frac{1}{h^f} e^{-\beta \mathscr{H}} \mathrm{d}\{p, q\} \qquad \Pr(\{p, q\}) = \frac{1}{Z_N} e^{-\beta \mathscr{H}}$$

For quantum or discrete systems, it is similar,

$$Z_N = \sum_{\text{states}} e^{-\beta E_{\text{state}}} \qquad \Pr(\text{state}) = \frac{1}{Z_N} e^{-\beta E_{\text{state}}}$$

We will see that as entropy connected to the different thermodynamic variables for the microcanonical ensemble, it is the partition function that serves this role for the canonical ensemble.

For instance, we have

$$\langle E \rangle = \int \frac{1}{h^n} \mathscr{H}(\{p, q\}) \Pr(\{p, q\}) \mathrm{d}\{p, q\}$$

Here is a little trick. First consider

$$\begin{aligned} \frac{\partial Z_N}{\partial \beta} &= \int \frac{1}{h^f} \frac{\partial}{\partial \beta} e^{-\beta \mathscr{H}} \mathrm{d}\{p, q\} \\ &= \int \frac{1}{h^f} (-\mathscr{H}) e^{-\beta \mathscr{H}} \mathrm{d}\{p, q\} \end{aligned}$$

Now,

$$
\begin{aligned}
-\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} &= \int \frac{1}{h^n}\mathscr{H}\frac{e^{-\beta\mathscr{H}}}{Z_N}\mathrm{d}\{p,q\} \\
&= \int \frac{1}{h^n}\mathscr{H}\Pr(\{p,q\})\mathrm{d}\{p,q\} \\
&= \langle E\rangle
\end{aligned}
$$

It might be more convenient to write

$$
\langle E\rangle = -\frac{\partial \ln Z_N}{\partial \beta}
$$

6.3 Energies

In the microcanonical ensemble we only had one fixed energy, the internal energy. In the canonical ensemble the energy is not fixed, and it depends on what $\langle E\rangle$ is equal to.

First we have to determine what variables we are controlling in our system.

Example 6.1. If we control the volume, then $\langle E\rangle = U$. More notable, in our derivations above, if the system was large enough for thermodynamics to apply, then we can $Z_N = \exp\left(-\frac{\langle E\rangle - TS}{k_B T}\right)$. This was derived without any additional assumptions regarding the system, so we can write the Helmholtz free energy $F = U - TS = \langle E\rangle - TS = -k_B T \ln Z_N$. ◊

Example 6.2. If we control the pressure, then $\langle E\rangle = H$, and the Gibbs free energy is $G = H - TS = \langle E\rangle - TS = -k_B T \ln Z_N$. ◊

6.4 Applications

There are a few benefits to using the canonical ensemble versus the microcanonical ensemble. For one, in the canonical ensemble the main variable of interest Z_N is obtained through integrating all of phase space $\mathrm{d}\{p,q\}$, whereas in the microcanonical ensemble we have integrate over a shell in the phase space.

The second benefit comes when we have a separable system, i.e. $\mathscr{H} = \mathscr{H}_a + \mathscr{H}_b$. In this case,

$$
\begin{aligned}
\exp(-\beta\mathscr{H}) &= \exp\left(-\frac{\mathscr{H}_a}{k_B T}\right)\exp\left(-\frac{\mathscr{H}_b}{k_B T}\right) \\
\Pr(\{p,q\}) &= \Pr(\{p,q\}_a)\Pr(\{p,q\}_b) \\
Z_N &= Z_a Z_b
\end{aligned}
$$

and so on. This is useful when we have a system made up of a number of similar but distinguishable non-interacting systems, where we simply have $Z_N = (Z_1)^N$. For indistinguishable systems, to account for double counting, we have $Z_N = \frac{(Z_1)^N}{N!}$.

Example 6.3 (Ideal gas)**.** We will consider an ideal gas in a container of length L_x. Bohr Sommerfield theory tells us that the momentum of the atoms $p = \frac{nh}{\lambda}$ so $2p_x L_x = nh$. Then the kinetic energy of a particle is

$$
E_x = \frac{p_x^2}{2m} = \frac{n^2 h^2}{8mL_x^2}.
$$

In all 3 dimensions,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right).$$

Then the partition function is given by

$$\begin{aligned} Z_1 &= \sum_{n_z=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_x=1}^{\infty} e^{-\beta E} \\ &= \sum_{n_z=1}^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_z^2}{L_z^2}\right) \sum_{n_y=1}^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_y^2}{L_y^2}\right) \sum_{n_x=1}^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_x^2}{L_x^2}\right) \end{aligned}$$

Typically, $n_x, n_y, n_z \gg 1$, so we can replace the summations with integrals. We also approximately use an integral starting from 0 instead of 1. Hence,

$$Z_1 \approx \int_0^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_z^2}{L_z^2}\right) \mathrm{d}n_z \int_0^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_y^2}{L_y^2}\right) \mathrm{d}n_y \int_0^{\infty} \exp\left(\beta \frac{h^2}{8m}\frac{n_x^2}{L_x^2}\right) \mathrm{d}n_x$$

The integrand is a Gaussian function, using the fact that $\int_{-\infty}^{\infty} \frac{1}{2\pi\sigma^2} \exp\left(-\frac{x^2}{2\sigma^2}\right)\mathrm{d}x = 1$, we have

$$Z_1 \approx \left(\sqrt{\frac{2\pi m}{\beta h^2}}\right)^3 L_x L_y L_z$$

For a particle at a given temperature T and of mass m, the de-Broglie wavelength of the particle is given by

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

So $Z_1 = \frac{V}{\lambda^3}$ where V is the volume of the box. Now, consider N identical particles, so we have

$$\begin{aligned} Z_N &= \frac{Z_1^N}{N!} \\ &= V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \frac{1}{N!}. \end{aligned}$$

At a certain volume the Helmholtz free energy is given by

$$\begin{aligned} F &= -k_B T \ln\left[V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \frac{1}{N!}\right] \\ &\approx -k_B T\left[N \ln\left(V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right) - N\ln N + N\right] \\ &= N k_B T\left[\ln\left(\frac{N}{V}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right) - 1\right] \end{aligned}$$

Recall that $S = -\left(\frac{\partial F}{\partial T}\right)_V$. So

$$\begin{aligned} S &= -N k_B\left[\ln\left(\frac{N}{V}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right) - 1\right] - N k_B T \frac{\partial}{\partial T}\left(-\frac{3}{2}\ln T\right) \\ &= -\frac{F}{T} + \frac{3}{2} N k_B \end{aligned}$$

Therefore from $U - TS = F$ we get

$$U = \frac{3}{2} N k_B T$$

as we expect. Next, recall $P = -\left(\frac{\partial F}{\partial V}\right)_T$. So

$$\begin{aligned} P &= -N k_B T \frac{\partial}{\partial V}(-\ln V) \\ &= \frac{N k_B T}{V} \end{aligned}$$

$\Diamond$

Example 6.4 (Two-level system)**.** We have a ground state of degeneracy 1 and an excited state at energy E with degeneracy g. For a single two-level system,

$$\begin{aligned} Z_1 &= \sum_{\text{states}} e^{-\beta E_{\text{state}}} \\ &= e^0 + g e^{-\beta E} \end{aligned}$$

Therefore the probability of being in a state is

$$\begin{aligned} \Pr(\text{state}) &= \frac{e^{-\beta E_{\text{state}}}}{Z_1} \\ &= \begin{cases} \dfrac{1}{1 + g e^{-\beta E}}, & \text{for } |0\rangle \\ \dfrac{1}{g^{\beta E} + g}, & \text{for any excited states} \end{cases} \end{aligned}$$

Now consider N distinguishable two-level systems, so $Z_N = Z_1^N$. The Helmholtz free energy is

$$\begin{aligned} F &= -k_B T \ln Z_N \\ &= -N k_B T \ln Z_1 \end{aligned}$$

We have $S = -\left(\frac{\partial F}{\partial T}\right)_V$ so

$$\begin{aligned} S &= N k_B \ln Z_1 + N k_B T \frac{-E g e^{-\beta E}}{1 + g e^{-\beta E}} \left(-\frac{1}{k_B T^2} \right) \\ &= N k_B \ln Z_1 + \frac{E g e^{-\beta E}}{1 + g e^{\beta E}} \frac{N}{T} \end{aligned}$$

Using $U - TS = F$ we have

$$\begin{aligned} U &= \frac{N E g e^{-\beta E}}{1 + g e^{-\beta E}} \\ &= N E \Pr(\text{excited state}). \end{aligned}$$

$\Diamond$

Example 6.5 (Polyatomic gases)**.** For a linear polyatomic gas molecule, we have

$$\mathscr{H} = \mathscr{H}_{\text{KE}} + \mathscr{H}_{\text{vib}} + \mathscr{H}_{\text{rot}}.$$

Though there are three possible axes of rotation, we do not really consider the z-axis, and we consider that as quantum mechanical spin instead of actual rotation. Recall the following properties of the angular momentum operator $\mathbf{L}$:

$$\mathbf{L}^2\Psi_{l,m} = l(l-1)\hbar^2\Psi_{l,m}$$
$$\mathbf{L}_z\Psi_{l,m} = m\hbar\Psi_{l,m}.$$

Furthermore we also have $\mathscr{H}_{\text{rot}} = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}$. For a linear molecule L_3 is effectively zero. With a bond length of r, we have $I_1 = I_2 = \mu r^2$ where μ is the reduced mass. Thus $\mathscr{H}_{\text{rot}} = \frac{\mathbf{L}_1^2+\mathbf{L}_2^2}{2I_1} = \frac{\mathbf{L}^2}{2I_1}$. The eigenenergies are thus $\frac{l(l+1)\hbar^2}{2I_1}$. The fact that the energy does not depend on m means that there is some degeneracy. Since $-l \leq m \leq l$, the degeneracy is $2l+1$.

Let $\theta_R = \frac{\hbar^2}{2I_1}$. The partition function is given by

$$\begin{aligned} Z &= \sum_{l,m} \exp\left(\frac{-l(l+1)\theta_R}{T}\right) \\ &= \sum_{l} (2l+1)\exp\left(\frac{-l(l+1)\theta_R}{T}\right) \end{aligned}$$

$\Diamond$

7 Grand canonical ensemble

In the grand canonical ensemble, we not only allow for the exchange of energy, but also the exchange of particles. The system is in contact with a particle reservoir characterised by chemical potential μ (and the heat bath has temperature T). In many ways μ is the direct analogue of T, it is a quantity that we get when two systems achieve equilibrium.

The energy of the combined system is composed of the energy of the system and the energy of the reservoir. From $\mathrm{d}U = T\mathrm{d}S + \mu\mathrm{d}N$ we have $\mu = \left(\frac{\partial U}{\partial N}\right)_S$. Total energy is hence

$$E = E_{i,N} + \mu N_{\text{res}}$$

where $E_{i,N}$ is the energy of the system in state i with N particles, and N_{res} is the number of particles in the reservoir. We express N_{res} in terms of the number of particles in the system N and the total number of particles N_{tot} as $N_{\text{res}} = N_{\text{tot}} - N$. Now μN_{tot} is a constant energy offset so we can just ignore it. This leaves us with

$$E = E_{i,N} - \mu N.$$

7.1 Grand partition function

In the grand canonical ensemble, the probability for finding the system in state i and number of particles N is similar to the canonical ensemble

$$\Pr(i,N) = \frac{1}{\Xi} e^{-\beta(E_{i,N}-\mu N)}$$

where Ξ is the *grand partition function.*

Ξ is also the normalisation constant. So

$$\Xi = \sum_{i,N} e^{-\beta(E_{i,N} - \mu N)}$$

Ξ does not depend on i or N since we have already summed across them. It will be a function of thermodynamic variables, usually μ and T.

Further simplification yields

$$\begin{aligned}\Xi(\mu, T, V) &= \sum_N e^{\beta\mu N} \sum_i e^{-\beta E_{i,N}} \\ &= \sum_N z^N Z(T, N, V)\end{aligned}$$

where Z is the canonical partition function and $z = e^{\beta\mu}$ is a quantity known as the *fugacity.*

As an example, the probability of finding the system with a certain quantity of particles is

$$\Pr(N) = \sum_i \Pr(i, N) = \frac{1}{\Xi} z^N Z(T, N, V).$$

7.2 Particle numbers

We perform a similar derivation as we did for the canonical ensemble and energy. Using the definition of mean,

$$\langle N \rangle = \sum_N N \Pr(N) = \frac{\sum_N N e^{\beta\mu N} Z}{\sum_N e^{\beta\mu N} Z}$$

Using a familiar partial derivative,

$$\frac{\partial}{\partial \mu} \ln \Xi = \frac{1}{\Xi} \frac{\partial \Xi}{\partial \mu} = \frac{1}{\Xi} \sum_N \beta N e^{\beta\mu N} Z.$$

Hence

$$\langle N \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T,V}$$

7.3 Thermodynamic variables

In the canonical ensemble the thermodynamic variables were related to the partition function Z directly through various energies. For the grand canonical ensemble, we will use an energy called the *grand potential*

$$\Phi(T, \mu, V) = -k_B T \ln \Xi(T, \mu, V).$$

In the thermodynamic limit, the N we have is close to $\langle N \rangle$. Thus

$$\ln \Xi = \ln \sum_N e^{\beta\mu N} Z \approx \ln \left(e^{\beta\mu \langle N \rangle} Z \right) = \ln e^{\beta\mu \langle N \rangle} + \ln Z$$

Therefore, suppose we control V and thus had $F = U - TS$,

$$\begin{aligned}\Phi &= -k_B T \ln e^{\beta\mu\langle N\rangle} - k_B T \ln Z \\ &= -\mu\langle N\rangle + \langle E\rangle - TS \\ &= F - \mu\langle N\rangle\end{aligned}$$

The interpretation of this is as follows. From the microcanonical to the canonical ensemble, we exchange control of temperature for control of entropy and obtain the Helmholtz free energy. Now we are exchanging control of particle number for control of chemical potential.

$$\begin{aligned}\mathrm{d}\Phi &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N - \mu\mathrm{d}N - N\mathrm{d}\mu \\ &= -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu\end{aligned}$$

7.4 Applications

Example 7.1. Imagine two classical gases separated by a partition, call them gas 1 and gas 2. They are at the same temperature, but can exchange particle number. Gas 1 has a potential energy per particle of 0 and gas 2 has a potential energy per particle of V_0. (This is a simple model of different gases in the atmosphere.)

Particles will be exchanged until they reach the same chemical potential μ. For gas 1,

$$\Phi_1 = F_1 - \mu N_1$$

where $F_1 = -k_B T \ln Z_N$ where $Z_N = \frac{Z_1^N}{N!}$ where $Z_1 = \frac{V}{\lambda^3}$ where λ is the de Broglie wavelength. This was derived for an ideal gas using the canonical ensemble so we will skip the derivation. All together,

$$\Phi_1 = N_1 k_B T\left(\ln \frac{N_1}{V}\lambda^3 - 1\right) - \mu N_1$$

where $n_1 = \frac{N_1}{V}$ is related to the density. We have

$$\begin{aligned}\mu_1 &= \left(\frac{\partial F_1}{\partial N_1}\right)_{V,T} \\ &= k_B T\big(\ln n_1\lambda_1^3 - 1\big) + \frac{N_1 k_B T}{N_1} \\ &= k_B T \ln n_1 \lambda_1^3\end{aligned}$$

In general for an ideal gas $\mu = k_B T \ln n\lambda^3$. We can also get a relation for n_1

$$n_1 = \frac{1}{\lambda^3} e^{\beta\mu}.$$

For gas 2, we need to account for the extra potential:

$$\Phi_2 = N_2 k_B T\big(\ln n_2\lambda^3 - 1\big) + N_2 V_0 - \mu N_2.$$

Again,

$$\begin{aligned}\mu_1 &= \left(\frac{\partial F_2}{\partial N_2}\right)_{V,T} \\ &= k_B T\big(\ln n_2\lambda_2^3 - 1\big) + V_0 + \frac{N_2 k_B T}{N_2} \\ &= k_B T \ln n_2 \lambda_2^3 + V_0.\end{aligned}$$

The expression for n_2 is given by

$$\frac{1}{\lambda^3} e^{\beta(\mu_2 - V_0)}$$

Thus in equilibrium, the densities of the gases are related by

$$\frac{n_1}{n_2} = \frac{\lambda_2^3}{\lambda_1^3} e^{V_0 \beta}$$

$\Diamond$

8 Quantum statistics

Bosons	Fermions
$\Psi(r_1, r_2) = \Psi(r_2, r_1)$	$\Psi(r_1, r_2) = -\Psi(r_2, r_1)$
Symmetric states	Anti-symmetric states
Bose-Einstein statistics	Fermi-Dirac statistics
Integer spin	Half-integer spin
photons, phonons, etc	electrons, protons, etc

There are also composite particles that can be bosons or fermions. For example the sodium atom with 23 nucleons and 11 electrons is a boson. The lithium atom with 6 nucleons and 3 electrons is a fermion.

8.1 Quantum statistics of two particles

If we have two particles in a box, using classical statistics we have

$$\begin{aligned} Z_2 &= \frac{Z_1^2}{2} \\ &= \frac{1}{2}\left(\sum_i e^{-\beta E_i}\right)^2 \\ &= \sum_{i \neq j} e^{-\beta(E_i + E_j)} + \frac{1}{2}\sum_i e^{-2\beta E_i} \end{aligned}$$

Assume the particles are fermions of the same spin, so they have anti-symmetric wave functions, which means that two fermions with the same spin cannot occupy the same position (set $r_1 = r_2$). Therefore the partition function is not correct.

$$\begin{aligned} Z_2 &= \sum_{\text{states}} e^{-\beta E_{\text{state}}} \\ &= \sum_{i \neq j} e^{-\beta(E_i + E_j)} \end{aligned}$$

Now assume that the particles are bosons of the same spin, so they have symmetric wave functions. There are no restrictions on the position that the particles are allowed to take. Therefore in this case

$$\begin{aligned} Z_2 &= \sum_{\text{states}} e^{-\beta E_{\text{state}}} \\ &= \sum_{i \neq j} e^{-\beta(E_i + E_j)} + \sum_i e^{-2\beta E_i} \end{aligned}$$

In general at a high temperature limit the first terms dominate, since it is more likely for particles to occupy different states.

8.2 Quantum statistics of N particles

The occupation number n_i refers to the number of particles that are occupying the i-th state. We can try first using the canonical ensemble.

$$\begin{aligned} Z &= \sum_{\text{states}} e^{-\beta E_{\text{state}}} \\ &= \sum_{\substack{\{n_i\} \\ \sum_i n_i = N}} e^{-\beta \sum_i n_i E_i} \\ &= \sum_{\substack{\{n_i\} \\ \sum_i n_i = N}} \left(\prod_i e^{-\beta n_i E_i} \right) \end{aligned}$$

This is an impossible sum to calculate.

We can try to remove the constraint on N and use the grand canonical ensemble instead.

$$\begin{aligned} \Xi &= \sum_N e^{-\beta \mu N} Z \\ &= \sum_N e^{-\beta \mu N} \sum_{\substack{\{n_i\} \\ \sum_i n_i = N}} e^{-\beta \sum_i n_i E_i} \\ &= \sum_{n_1} \sum_{n_2} \cdots e^{\beta n_1 (\mu - E_1)} e^{\beta n_2 (\mu - E_2)} \cdots \\ &= \prod_i \left(\sum_{n_i} e^{\beta n_i (\mu - E_i)} \right). \end{aligned}$$

8.3 Fermions

For fermions $n_i = 0, 1$. Therefore

$$\begin{aligned} \Xi &= \prod_i \left(\sum_{n_i = 0,1} e^{\beta n_i (\mu - E_i)} \right) \\ &= \prod_i \left(1 + e^{\beta(\mu - E_i)} \right). \end{aligned}$$

We also have

$$\begin{aligned}\langle N\rangle &= \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu}\\ &= \frac{1}{\beta}\frac{\partial}{\partial \mu}\sum_i \ln\left(1+e^{\beta(\mu-E_i)}\right)\\ &= \frac{1}{\beta}\sum_i \frac{\beta e^{\beta(\mu-E_i)}}{1+e^{\beta(\mu-E_i)}}\\ &= \sum_i \frac{1}{e^{\beta(E_i-\mu)}+1}\end{aligned}$$

Since $\sum_i n_i = N$, we also have $\sum_i \langle n_i\rangle = \langle N\rangle$, which gives us the Fermi-Dirac distribution

$$\langle n_i\rangle = \frac{1}{e^{\beta(E_i-\mu)}+1}$$

The Fermi energy E_F is μ at $T=0$. At $T=0$ we can see that μ is the point where the probability of occupying a given state is $\frac{1}{2}$. We will dive in deeper to the case of $T=0$.

We can describe metals as a free electron gas. We will assume an isolated system with N free fermions. It turns out that the wavefunction is given by

$$\Psi(\vec{r},\vec{s}) = \frac{1}{\sqrt{V}}e^{-ik\vec{r}}\psi_{\text{spin}}(\vec{s})$$

Periodicity in our lattice means that

$$\Psi(\vec{r}+n_xL_x\hat{\mathbf{x}}+n_yL_y\hat{\mathbf{y}}+n_zL_z\hat{\mathbf{z}}) = \Psi(\vec{r})$$

so the wavevector is

$$\vec{k} = n_x\frac{2\pi}{L_x}\hat{\mathbf{x}} + n_y\frac{2\pi}{L_y}\hat{\mathbf{y}} + n_z\frac{2\pi}{L_z}\hat{\mathbf{z}}$$

We want to find the density of k-states. Density is the number of states per unit volume. So

$$D = \frac{1}{\frac{2\pi}{L_x}\frac{2\pi}{L_y}\frac{2\pi}{L_z}} = \frac{V}{(2\pi)^3}$$

Fermions will fill up the lower energy states from 0 up to $E_F = \frac{\hbar^2k_F^2}{2m}$ with a radius in k-space of k_F. Thus the total number of fermions in this sphere is

$$N = D\times\frac{4}{3}\pi k_F^3\times 2$$

The factor of 2 here is accounting for both spin up and spin down states. Altogether we obtain the following expression.

$$N = \frac{V}{3\pi^2}k_F^3$$

The Fermi wavefactor is therefore $k_F = \left(3\pi^2\frac{N}{V}\right)^{\frac{1}{3}}$, from there we also have the Fermi energy $E_F = \frac{\hbar^2k_F^2}{2m}$.

For a more general case, the number of states up to some arbitrary energy E is

$$\begin{aligned} N_E &= D \times \frac{4}{3}\pi k^3 \times 2 \\ &= \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}E\right)^{\frac{3}{2}} \end{aligned}$$

The density of states is thus

$$\begin{aligned} D(E) &= \frac{\mathrm{d}N_E}{\mathrm{d}E} \\ &= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \end{aligned}$$

The area under the curve $D(E)\langle n\rangle$ gives us N which is easier to calculate for $T \neq 0$ (we assumed a sphere for the Fermi surface which may not hold for higher temperatures). A few interesting quantities. Total energy:

$$E = \int_0^{E_F} ED(E)\mathrm{d}E = \frac{3}{5}NE_F$$

Degeneracy pressure:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,S} = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \frac{2}{5}\frac{N}{V}E_F$$

8.4 Bosons

Let us consider photons. In a box, light exists as a combination of standing waves. These standing waves are also called *normal modes*. Each normal mode's energy has two quadratic degrees of freedom, associated with the electric and magnetic fields. So for k normal modes, we have

$$U = 2\sum_k k_B T.$$

If we assume that the modes are very close together, then we can approximate the sum as an integral,

$$\begin{aligned} U &= 2\sum_k k_B T \\ &= 2D(k)\int k_B T \mathrm{d}^3 k \\ &= \frac{V}{4\pi^3}k_B T \iiint k^2 \sin\theta \mathrm{d}k\mathrm{d}\theta\mathrm{d}\phi \\ &= \frac{V}{\pi^2}k_B T \int_0^\infty k^2 \mathrm{d}k \\ &= \frac{V}{\pi^2 c^3}k_B T \int_0^\infty \omega^2 \mathrm{d}\omega \end{aligned}$$

Since we have $\frac{U}{V} = \int_0^\infty u(w)\mathrm{d}\omega$ where $u(w)$ is the energy density,

$$u(\omega) = \frac{k_B T}{\pi^2 c^3}\omega^2$$

This is what is known as the ultraviolet catastrophe. Planck "solved" this problem by supposing that harmonic oscillator modes do not form a continuous spectrum of energy, but rather each node has an energy of $n\hbar\omega$. We have

$$\begin{aligned} Z_1 &= \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} \\ &= \frac{1}{1-e^{-\beta\hbar\omega}} \end{aligned}$$

So the average energy of a single harmonic oscillator is given by

$$\begin{aligned} \langle E\rangle &= -\frac{1}{Z_1}\frac{\partial Z_1}{\partial\beta} \\ &= \frac{\hbar\omega e^{-\beta\hbar\omega}}{e^{-\beta\hbar\omega}-1} \\ &= \frac{\hbar\omega}{e^{-\beta\hbar\omega}-1} \\ &= \hbar\omega\langle n\rangle \end{aligned}$$

where here we call $\langle n\rangle$ the Planck distribution. Notice how we got away with using just the canonical ensemble. This is not a mistake, indeed, if we set $\mu = 0$ in the Bose-Einstein distribution $\langle n\rangle_{BE} = \frac{1}{e^{\beta(E-\mu)}-1}$ we get exactly the Planck distribution. This means that $\mu = \left(\frac{\partial U}{\partial N}\right)_S = 0$, which in turn means that it does not cost any energy to create or destroy a photon.

Let us continue. First we are interested in the photon density $\frac{N}{V}$. Again we apply the same trick

$$\begin{aligned} N &= 2\sum_k n_k \\ &= 2\frac{V}{(2\pi)^3}\int \frac{1}{e^{\beta E_k}-1}\mathrm{d}^3k \\ \frac{N}{V} &= \frac{1}{\pi^2}\int_0^\infty \frac{k^2}{e^{\beta\hbar ck}-1}\mathrm{d}k \\ &= \frac{1}{\pi^2c^3}\int_0^\infty \frac{\omega^2}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega \\ &= \frac{1}{\pi^2c^3}\left(\frac{1}{\beta\hbar}\right)^3\int_0^\infty \frac{x^2}{e^x-1}\mathrm{d}x \\ &\approx 0.24\left(\frac{k_BT}{\hbar c}\right)^3. \end{aligned}$$

Where we have made the substitution $x = \beta\hbar\omega$ and $\mathrm{d}\omega = \frac{\mathrm{d}x}{\beta\hbar}$ to make the integral dimensionless.

Now we move on to the energy density

$$\begin{aligned}
U &= 2\sum_k E_k n_k \\
&= 2\sum_k \frac{E_k}{e^{\beta E_k}-1} \\
&= \frac{V}{4\pi^3}\int \frac{E_k}{e^{\beta E_k}-1}\mathrm{d}^3k \\
&= \frac{V}{\pi^2}\int_0^\infty \frac{\hbar c k^3}{e^{\beta\hbar c k}-1}\mathrm{d}k \\
&= \frac{V\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega \\
\frac{U}{V} &= \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega \\
&= \frac{\hbar}{\pi^2 c^3}\left(\frac{1}{\beta\hbar}\right)^4\int_0^\infty \frac{x^3}{e^x-1}\mathrm{d}x \\
&= \frac{\pi^2(k_B T)^4}{15(\hbar c)^3}
\end{aligned}$$

which is also known as the Stefan-Boltzmann law. We also have

$$u(w) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}.$$

which is also known as the Planck spectral density.

We may also be interested in the blackbody radiation pressure $P = -\left(\frac{\partial F}{\partial V}\right)_T$. Since the modes are all distinguishable, we have $F = -k_B T 2\sum_k \ln Z_k$. Furthermore we are given that $E_k \propto \frac{1}{V^{1/3}}$, and so $\frac{\partial E_k}{\partial V} = -\frac{1}{3}\frac{E_k}{V}$. Then

$$\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_T \\
&= -\frac{\partial}{\partial V}2k_B T\sum_k \ln\left(1-e^{\beta E_k}\right) \\
&= -2\sum_k \frac{\frac{\partial E_k}{\partial V}e^{-\beta E_k}}{1-e^{-\beta E_k}} \\
&= \frac{1}{3V}\sum_k \frac{2E_k}{e^{\beta E_k}-1} \\
&= \frac{1}{3}\frac{U}{V}.
\end{aligned}$$

9 Appendix

9.1 Partial derivatives

Some relations.

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

A simple derivation of the chain rule:

$$\begin{aligned}
\mathrm{d}x &= \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z \\
\mathrm{d}y &= \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z \\
\implies \mathrm{d}x &= \frac{\partial x}{\partial y}\frac{\partial y}{\partial x}\mathrm{d}x + \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\mathrm{d}z + \frac{\partial x}{\partial z}\mathrm{d}z \\
\implies -1 &= \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\frac{\partial z}{\partial x}
\end{aligned}$$

Let $w = w(x, y, z)$. Then

$$\left(\frac{\partial x}{\partial y}\right)_w = \frac{\left(\frac{\partial x}{\partial z}\right)_w}{\left(\frac{\partial y}{\partial z}\right)_w}.$$

We also have

$$\left(\frac{\partial x}{\partial y}\right)_w = \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_w.$$

Finally

$$\frac{\partial^2 y}{\partial z \partial x} = \left[\frac{\partial}{\partial z}\left(\frac{\partial y}{\partial x}\right)_z\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial y}{\partial z}\right)_x\right]_z.$$

9.2 Equations of state

We call a function $S = S(x, y)$ iff $\mathrm{d}S$ is an exact differential. In other words, we can write

$$\mathrm{d}S = \left(\frac{\partial S}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial S}{\partial y}\right)_x \mathrm{d}y$$

So work is not a state function.

Suppose we are given $S = A\,\mathrm{d}x + B\,\mathrm{d}y$. How do we find the expression for S? First, we can integrate A:

$$\begin{aligned}
\left(\frac{\partial S}{\partial x}\right)_y &= A \\
S &= \int A\,\mathrm{d}x + f(y)
\end{aligned}$$

Then, differentiate it again and equate it to B.

$$B = \left(\frac{\partial S}{\partial y}\right)_x = \frac{\partial}{\partial y}\left[\int A\,\mathrm{d}x + f(y)\right]$$

Using this, we can find an expression for $f(y)$,

$$\begin{aligned}\frac{\partial f}{\partial y} &= B - \frac{\partial}{\partial y}\int A\,\mathrm{d}x \\ f &= \int\left[B - \frac{\partial}{\partial y}\int A\,\mathrm{d}x\right]\mathrm{d}y\end{aligned}$$

Then now we can integrate B and find the true expression for S.

$$S = \int A\,\mathrm{d}x + \int\left[B - \frac{\partial}{\partial y}\int A\,\mathrm{d}x\right]\mathrm{d}y$$

Example 9.1. For some gas, we are given

$$\begin{aligned}A &= \left(\frac{\partial P}{\partial T}\right)_V = \frac{NK_B}{V - Nb} \\ B &= \left(\frac{\partial P}{\partial V}\right)_T = -\frac{NK_BT}{(V-Nb)^2} + \frac{2aN^2}{V^3},\end{aligned}$$

and that the gas becomes an ideal gas for large T and V, find the equation of state for this gas.

First, integrate A:

$$P = \int \frac{NK_B}{V - Nb}\,\mathrm{d}T = \frac{NK_BT}{V - Nb} + f(V).$$

Partial derivative with respect to V:

$$B = \frac{\partial P}{\partial V} = \frac{\partial}{\partial V}\left[\frac{NK_BT}{V - Nb} + f(V)\right] = \frac{NK_BT}{(V-Nb)^2} + \frac{\partial f}{\partial V}$$

Then we see directly that

$$\begin{aligned}\frac{\partial f}{\partial V} &= \frac{2aN^2}{V^3} \\ f &= -\frac{aN^2}{V^2} + C\end{aligned}$$

Therefore we get that

$$P = \frac{NK_BT}{V - Nb} - \frac{aN^2}{V^2} + C.$$

Plugging in the given boundary condition, when $T, V \to \infty$ we need $P = \frac{NK_BT}{V}$, so $C = 0$. $\Diamond$

9.3 Probability

Sometimes we simply cannot keep track of something because it is too difficult to do so, or because it is inherently random. So we have to turn to probability.

Given a random variable x and the probability density function p, we first note that $p(x_0)$ does not give us the probability for $x = x_0$. Rather, it is defined as

$$\Pr[x_1 < x < x_2] = \int_{x_1}^{x_2} p(x)\,\mathrm{d}x\,.$$

We also have the *cumulative probability* at some point, which is given by

$$P(x) = \int_{-\infty}^{x} p(x)\,\mathrm{d}(x)$$

Furthermore, we also have some statistics. The mean is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} xp(x)\,\mathrm{d}x \qquad \langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)p(x)\,\mathrm{d}x$$

We also have the variance, which is the square of the standard deviation σ:

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