

Chapter 3. Boltzmann distribution and Helmholtz free energy

1 The Boltzmann factor

In this chapter we are going to consider systems that are in thermal contact with a *heat bath* or *reservoir*. The reservoir can be any system that is very much larger than the system of interest. The combined system of the reservoir $\mathcal{R}$ and the system of interest $\mathcal{S}$ forms a single isolated system. We will show that for the purpose of studying $\mathcal{S}$ the only important property of the reservoir is its temperature.

We would like to know the probability that the system $\mathcal{S}$ is in a particular quantum state s of energy ϵ_s . Using the fundamental hypothesis this is just

$$P(s) = \frac{g_{\mathcal{R}}(U_0 - \epsilon_s)}{\sum_{s'} g_{\mathcal{R}}(U_0 - \epsilon_{s'})},$$

where U_0 is the total energy of the system and the sum is over all accessible states of the system. The denominator in this expression is the same for all s , so that we will ignore it for the present and simply write $P(s) \propto g_{\mathcal{R}}(U_0 - \epsilon_s)$.

Now since $\mathcal{R} \gg \mathcal{S}$, $\epsilon_s \ll U_0$, so that we may use an approximation for the dependence of $g_{\mathcal{R}}$ on ϵ_s . But $g_{\mathcal{R}}$ is an extremely rapidly increasing function of U . We get a much better result by expanding $\sigma_{\mathcal{R}} = \ln g_{\mathcal{R}}$ rather than $g_{\mathcal{R}}$ itself. Hence use

$$\sigma_{\mathcal{R}}(U_0 - \epsilon_s) \simeq \sigma_{\mathcal{R}}(U_0) - \epsilon_s \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U} \right) \Big|_{U=U_0} = \sigma_{\mathcal{R}}(U_0) - \frac{\epsilon_s}{\tau},$$

where τ is the temperature of the reservoir $\mathcal{R}$, giving

$$g_{\mathcal{R}}(U_0 - \epsilon_s) \simeq g_{\mathcal{R}}(U_0) \exp \left(-\frac{\epsilon_s}{\tau} \right).$$

The factor $g_{\mathcal{R}}(U_0)$ is a constant, so we have shown that

$$P(s) \propto \exp \left(-\frac{\epsilon_s}{\tau} \right),$$

a result that is used widely in statistical physics. The exponential factor is known as the *Boltzmann factor*.

A brief inspection will show that this result depends critically on the fact that we expanded $\sigma_{\mathcal{R}}$ rather than $g_{\mathcal{R}}$. Why not the latter? Let us take a typical case of the ideal gas where $g(N, U) = KU^{\frac{3N}{2}}$, for some constant K . Expanding $\ln g$ first, we get

$$\ln g(U_0 - \epsilon) = \ln K + \frac{3N}{2} \ln(U_0 - \epsilon) \simeq \ln K + \frac{3N}{2} \left(\ln U_0 - \frac{\epsilon}{U_0} \right).$$

This approximation is reasonable as long as $\epsilon \ll U_0$, which is precisely what we have assumed. Exponentiating the result gives

$$g(U_0 - \epsilon) \simeq g(U_0) \exp \left(-\frac{3N\epsilon}{2U_0} \right).$$

Now expand g directly,

$$g(U_0 - \epsilon) \simeq g(U_0) - \epsilon \frac{3N}{2} KU_0^{\frac{3N}{2}-1} = g(U_0) \left(1 - \frac{3N\epsilon}{2U_0} \right).$$

This is what we would have obtained from the former approximation if $\epsilon \ll U_0/N$. In a system of N particles U_0/N is the typical energy of a single particle. While the former approximation is satisfied by definition for a system in contact with a reservoir, the latter is almost never going to be satisfied for the states of interest.

1.1 The partition function

Since we have shown the $P(s) \propto \exp(-\epsilon_s/\tau)$, we can now give the probability that the system $\mathcal{S}$ is in the state s as

$$P(s) = \frac{\exp(-\frac{\epsilon_s}{\tau})}{\sum_{s'} \exp(-\frac{\epsilon_{s'}}{\tau})},$$

where we have used the Boltzmann approximation and simply cancelled all the constant factors of $g_{\mathcal{R}}(U_0)$. This expression now depends only on the temperature τ of the reservoir. Note again that the sum is over all states of the system $\mathcal{S}$.

The normalization factor

$$Z(\tau) = \sum_s \exp\left(-\frac{\epsilon_s}{\tau}\right)$$

in the denominator for $P(s)$ turns out to be a very useful function in its own right. It is known as the *partition function*.

(Terminology note: an ensemble of isolated systems is often referred to as a *microcanonical ensemble*. An ensemble of systems in contact with heat baths at some fixed temperature is known as a *canonical ensemble*. In this terminology Z is known as the *canonical partition function*. The multiplicity σ might be referred to as the microcanonical partition function, and later in the course we will come to the *grand canonical ensemble* and its associated partition function.)

In terms of Z , then

$$P(s) = \frac{\exp(-\frac{\epsilon_s}{\tau})}{Z},$$

and we can use this to calculate the mean value of any physical parameter of the system. One quantity of considerable interest is the mean value of the energy of the system $\mathcal{S}$, which we will now write as U ,

$$U = \langle \epsilon \rangle = \sum_s \epsilon_s P(s) = \frac{1}{Z} \sum_s \epsilon_s \exp\left(-\frac{\epsilon_s}{\tau}\right) = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right)_N.$$

We can obtain similar expressions for $\langle \epsilon^m \rangle$ for any integer m in terms of the partial derivatives of Z , so that Z is a generating function for the moments of the energy. (Note that these expressions are much neater when Z is treated as a function of $\beta = 1/\tau$.)

1.2 Example: a two state system

Consider a one particle system with two states, one of energy 0 and the other of energy ϵ , in contact with a reservoir at temperature τ . The partition function of this system is

$$Z = \exp\left(-\frac{0}{\tau}\right) + \exp\left(-\frac{\epsilon}{\tau}\right) = 1 + \exp\left(-\frac{\epsilon}{\tau}\right),$$

so that the average energy is

$$U = \frac{\epsilon \exp(-\frac{\epsilon}{\tau})}{1 + \exp(-\frac{\epsilon}{\tau})} = \frac{\epsilon}{\exp(\frac{\epsilon}{\tau}) + 1}.$$

The *heat capacity* of the system at constant volume is the energy required to raise its temperature by one unit, *i.e.*

$$C_V = \left(\frac{\partial U}{\partial \tau} \right)_V = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_V,$$

(the latter being the definition), so that

$$C_V = \left(\frac{\epsilon}{\tau} \right)^2 \frac{\exp\left(\frac{\epsilon}{\tau}\right)}{\left[\exp\left(\frac{\epsilon}{\tau}\right) + 1\right]^2}.$$

This is dimensionless. See the plot above. In more conventional units,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = k_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{\exp\left(\frac{\epsilon}{k_B T}\right)}{\left[\exp\left(\frac{\epsilon}{k_B T}\right) + 1\right]^2},$$

which has the dimensions of energy per Kelvin.

The *specific heat* is the heat capacity per unit mass of a system.

The peak in the heat capacity is called a Schottky anomaly. For $\tau \gg \epsilon$

$$C_V \simeq \left(\frac{\epsilon}{2\tau} \right)^2,$$

and for $\tau \ll \epsilon$

$$C_V \simeq \left(\frac{\epsilon}{\tau} \right)^2 \exp\left(-\frac{\epsilon}{\tau}\right),$$

so that C_V vanishes rapidly as $\tau \rightarrow 0$.

1.3 Reversible processes

When we make a change to a system it will not generally remain close to its equilibrium state while the change is occurring. If the change is made in such a way that the system does remain infinitesimally close to thermal equilibrium throughout, then the change is said to be *reversible*. If this is not the case, then the process of change is said to be irreversible. The significance of a reversible change is that we can describe it using thermal equilibrium values for the system.

Consider an insulated tube of ideal gas with a plunger in one end. We can change the volume of the gas by moving the plunger. If we move the plunger slowly into the tube then the gas will be compressed adiabatically — its total entropy will remain fixed during the compression. On the other hand, if the plunger is pushed too quickly a shock wave propagates into the tube dissipating energy and ultimately increasing the entropy of the final state.

Reversible changes do not have to conserve the entropy in general. The rate of change will usually distinguish reversible processes from irreversible ones (though not always). The actual rate of change required to make a process reversible is highly dependent on the system involved.

2 Pressure

As we have mentioned before, the definition of the temperature gives

$$\tau = \left(\frac{\partial U}{\partial \sigma} \right)_V,$$

where now we are allowing for a volume dependence in the energy U (and we will ignore the N dependence for the moment). This equation states that, when all other parameters of a system remain fixed, the change in the energy of the system associated with a change in the entropy is $dQ = \tau d\sigma$. In other words, this is the change in thermal energy of a system

The energy of a physical system may also be changed by altering the other parameters of the system. In particular, we consider the change in energy associated with a change in the volume of the system. Take the case of a thermally isolated system bounded on one side by a plane wall of area A . If the wall moves outward (perpendicular to itself) by a distance dx , then the volume of the system increases by $dV = Adx$. If the pressure exerted by the system on the wall is p , then the mechanical work done on the wall by the system is $dW = pAdx = pdV$. Since energy is conserved, this must be the energy loss from the system, *i.e.*

$$dU = \left(\frac{\partial U}{\partial V} \right)_{\sigma} dV = -pdV,$$

so that the pressure is given by

$$p = - \left(\frac{\partial U}{\partial V} \right)_{\sigma}.$$

We have glossed over a subtlety here. When we change the volume (or any other parameter) of the system the energies of the various (quantum) states of the system will change — by differing amounts. For example, the energy levels for a particle in a box are proportional to

$$\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2},$$

for positive integer triples (n_x, n_y, n_z) . If we change, say, L_x slowly the quantum numbers (n_x, n_y, n_z) remain fixed, so that the change in energy of a state will depend on the value of n_x . This means that the multiplicity of a configuration of the system will change when L_x changes. However, it is not difficult to see that the change in the multiplicity could be countered by adjusting the allowed energy spread of the system by a suitable amount. But we have already argued that for any reasonable choice, the value of the energy spread makes no significant difference to the value of σ . In short, because of the incredibly large numbers involved, the entropy does remain fixed when the volume of an isolated system is changed.

We can summarize these results by writing

$$dU = \left(\frac{\partial U}{\partial \sigma} \right)_{V} d\sigma + \left(\frac{\partial U}{\partial V} \right)_{\sigma} dV = \tau d\sigma - pdV,$$

when U is considered to be $U(V, \sigma)$. Rearranging this, we may write

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV = \left(\frac{\partial \sigma}{\partial U} \right)_{V} dU + \left(\frac{\partial \sigma}{\partial V} \right)_{U} dV,$$

where now we are taking $\sigma = \sigma(U, V)$. We deduce that

$$\left(\frac{\partial \sigma}{\partial V} \right)_{U} = \frac{p}{\tau}.$$

The result

$$dU = \tau d\sigma - pdV = TdS - pdV,$$

will be known as the *thermodynamic identity*. It is a differential statement of the 1st law of thermodynamics, that energy is conserved. It clearly separates the energy exchanges that a system can undergo into a mechanical part (pdV) and a thermal part, the *heat* $dQ = \tau d\sigma$.

Helmholtz free energy

The quantity

$$F = U - \tau\sigma,$$

is defined to be the *Helmholtz free energy*. If we consider F_S for a system in contact with a reservoir at temperature τ , then regarding σ_S as a function of U_S , V_S , N_S , *etc.* ,

$$F_S = F_S(N_S, V_S, U_S, \tau).$$

Fixing N_S , V_S , *etc.* (τ is fixed by the reservoir) and considering F_S as a function of U_S alone, we see that F_S has an extremum at the equilibrium solution for U_S , since

$$dF_S = dU_S - \tau \left(\frac{\partial \sigma_S}{\partial U_S} \right)_{N_S, V_S} dU_S,$$

which is 0 for the equilibrium value of U_S .

We can show that the extremum is a minimum by considering the total entropy of the system plus reservoir,

$$\sigma = \sigma_R + \sigma_S \simeq \sigma_R(U_0) - \frac{1}{\tau} U_S + \sigma_S(U_S) = \sigma_R(U_0) - \frac{F_S}{\tau}.$$

The total entropy σ has a maximum for the equilibrium distribution of energy between the reservoir and S and the temperature τ is fixed, so we see that F_S considered as a function of U_S must take on its minimum value in equilibrium.

2.1 The binary magnetic system again

For the binary system

$$\sigma(s) \simeq - \left(\frac{1}{2}N + s \right) \ln \left(\frac{1}{2} + \frac{s}{N} \right) - \left(\frac{1}{2}N - s \right) \ln \left(\frac{1}{2} - \frac{s}{N} \right)$$

(where we have dropped some negligible terms in the entropy and where we are no longer using the approximation $s \ll N$). The Helmholtz free energy (also known as the Landau function for magnetic systems) is then

$$F_L(\tau, s, B) = -2smB + \left(\frac{1}{2}N + s \right) \tau \ln \left(\frac{1}{2} + \frac{s}{N} \right) + \left(\frac{1}{2}N - s \right) \tau \ln \left(\frac{1}{2} - \frac{s}{N} \right).$$

When this is a minimum with respect to s (U) it becomes equal to the equilibrium free energy

$$F(\tau, B) = F_L(\tau, \langle s \rangle, B).$$

Looking for the minimum

$$\left(\frac{\partial F_L}{\partial s} \right)_{\tau, B} = 0 = -2mB + \tau \ln \frac{N + 2s}{N - 2s},$$

so that the equilibrium value for the spin excess is

$$\langle 2s \rangle = N \frac{\exp \left(\frac{2mB}{\tau} \right) - 1}{\exp \left(\frac{2mB}{\tau} \right) + 1} = N \tanh \left(\frac{mB}{\tau} \right).$$

The magnetization M is defined as the magnetic moment per unit volume, so that

$$M = \frac{\langle 2s \rangle m}{V} = mn \tanh \left(\frac{mB}{\tau} \right),$$

where n is the number of spins per unit volume in the system.

The equilibrium free energy can be calculated directly from this, but it is easier to get F from the result $F = -\tau \ln Z$ which we will prove shortly. For one magnet

$$Z = 2 \cosh \left(\frac{mB}{\tau} \right),$$

and for N independent magnets we just raise this to the power N , so that

$$F_L = -N\tau \ln \left[2 \cosh \left(\frac{mB}{\tau} \right) \right].$$

2.2 Differential relations

From now on, when we refer to F we will be referring to its equilibrium value. This fixes the value of U_S and σ_S in terms of the other parameters of the system and τ . The differential of F is then

$$dF = dU - \tau d\sigma - \sigma d\tau = -\sigma d\tau - p dV,$$

where we have used the thermodynamic identity. It follows that

$$\left(\frac{\partial F}{\partial \tau} \right)_V = -\sigma \quad \text{and} \quad \left(\frac{\partial F}{\partial V} \right)_\tau = -p.$$

The latter relationship shows that F behaves as the effective energy available in the system under an isothermal change (τ fixed; compare the similar result for an adiabatic change).

KK note that we can use the definition of F to write

$$p = - \left(\frac{\partial U}{\partial V} \right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V} \right)_\tau,$$

splitting the pressure into 2 parts. The first term is the “energy pressure” and is very important in solids, while the second term, the “entropy pressure” is far more important in gases and elastic polymers.

2.3 A Maxwell relation

The mixed second derivatives of F must be equal, so that we get the identity

$$-\frac{\partial^2 F}{\partial V \partial \tau} = \left(\frac{\partial \sigma}{\partial V} \right)_\tau = -\frac{\partial^2 F}{\partial \tau \partial V} = \left(\frac{\partial p}{\partial \tau} \right)_V.$$

This is one of a series of similar relationships.

2.4 F as a Legendre transform

Since $\tau = (\partial U / \partial \sigma)_{N,V}$, we can write the definition of the Helmholtz free energy as

$$F = U - \sigma \left(\frac{\partial U}{\partial \sigma} \right)_{N,V},$$

(for the equilibrium value of F), which is a Legendre transform of U with respect to σ . Using the partial derivatives we have deduced above, we can also write

$$U = F - \tau \left(\frac{\partial F}{\partial \tau} \right)_{N,V},$$

so that the inverse of the Legendre transform is another Legendre transform, this time with respect to

$$\tau = \left(\frac{\partial U}{\partial \sigma} \right)_{N,V}.$$

2.5 Relating F to Z

We will consider a system where the energy of any given state is a function of the volume. (The argument can be carried through much more generally.) We want to know how the energy of the system changes if we change the volume. Since the probability that the system is in a state s is

$$P(s) = \frac{1}{Z} \exp \left(-\frac{\epsilon_s}{\tau} \right),$$

the mean value of $\partial \epsilon_s / \partial V$ is

$$\left\langle \frac{\partial \epsilon_s}{\partial V} \right\rangle = \sum_s P(s) \frac{\partial \epsilon_s}{\partial V} = \frac{1}{Z} \sum_s \frac{\partial \epsilon_s}{\partial V} \exp \left(-\frac{\epsilon_s}{\tau} \right) = -\tau \left(\frac{\partial \ln Z}{\partial V} \right)_\tau.$$

But the average change of energy of a state of the system when V is changed by dV is $-pdV$ (and more generally

$$\left\langle \frac{\partial \epsilon_s}{\partial x} \right\rangle = -Q_x$$

— this is essentially the definition that distinguishes a mechanical interaction with the system from a thermal one), so that

$$\left(\frac{\partial \ln Z}{\partial V} \right)_\tau = \frac{p}{\tau}.$$

We can now evaluate the differential of $\ln Z$ (regarding it as a function of τ and V alone)

$$d \ln Z = \left(\frac{\partial \ln Z}{\partial \tau} \right)_V d\tau + \left(\frac{\partial \ln Z}{\partial V} \right)_\tau dV = \frac{U}{\tau^2} d\tau + \frac{p}{\tau} dV = -d \left(\frac{U}{\tau} \right) + \frac{1}{\tau} dU + \frac{p}{\tau} dV,$$

so that

$$d \left(\ln Z + \frac{U}{\tau} \right) = d\sigma.$$

To within an additive constant this gives

$$\sigma = \ln Z + \frac{U}{\tau}.$$

We can verify that the additive constant is zero by noting that for $\tau \rightarrow 0$ the system goes into its ground state of energy U_0 , so that

$$\sigma \rightarrow \sigma_0 = \ln g(U_0),$$

while

$$\ln Z \rightarrow \ln \left[g(U_0) \exp \left(-\frac{U_0}{\tau} \right) \right] = \sigma_0 - \frac{U_0}{\tau},$$

all other terms in the sum for Z being negligible.

Note that this result could be proved in similar fashion to the extensivity of the entropy. We can rewrite the sum for Z as

$$Z = \sum_{\epsilon} g(\epsilon) \exp \left(-\frac{\epsilon}{\tau} \right),$$

and then noting that g is a very rapidly increasing function of ϵ , while the Boltzmann factor is very rapidly decreasing, we could again show that there is a well defined peak in the terms of Z . The peak term is

$$g(U) \exp \left(-\frac{U}{\tau} \right),$$

and, as in the sum for the entropy, there will be about N^p terms that contribute significantly to the sum for Z . When we take the log this factor is negligible and end up with

$$\ln Z = \ln g(U) - \frac{U}{\tau} = \sigma - \frac{U}{\tau},$$

as we found above.

We now have

$$F = U - \sigma\tau = -\tau \ln Z.$$

Note the parallel here. We have transformed g (strictly $\mathcal{D}$) by a Laplace transformation with respect to U to get Z (look at the definition) and we have made a Legendre transform of U with respect to σ to get F , while

$$\sigma = \ln g \quad \text{and} \quad F = -\tau \ln Z.$$

3 The ideal gas

Consider a system consisting of a single particle (atom) of mass M inside a cubical box of volume $V = L^3$. The possible states of the particle are given by the eigensolutions of the Schrodinger equation

$$-\frac{\hbar^2}{2M} \nabla^2 \psi = \epsilon \psi.$$

If the walls of the box are regarded as infinite steps in the potential then the wavefunction must vanish there, so that for a box in the first octant with one vertex on the origin the solutions are

$$\psi(x, y, z) = A \sin \left(\frac{n_x \pi x}{L} \right) \sin \left(\frac{n_y \pi y}{L} \right) \sin \left(\frac{n_z \pi z}{L} \right),$$

where (n_x, n_y, n_z) are positive integers. The energy of this state is

$$\epsilon_{\mathbf{n}} = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2).$$

The partition function for this system is

$$\begin{aligned}
Z_1 &= \sum_{n_x, n_y, n_z} \exp \left[-\frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2ML^2\tau} \right] \\
&\simeq \int_0^\infty \int_0^\infty \int_0^\infty dn_x dn_y dn_z \exp \left[-\frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2ML^2\tau} \right] \\
&= \left[\int_0^\infty dn \exp \left(-\frac{\hbar^2 \pi^2 n^2}{2ML^2\tau} \right) \right]^3 = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}} L^3 = n_Q V = \frac{n_Q}{n},
\end{aligned}$$

where the *quantum concentration* is defined as

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}},$$

and the concentration is $n = 1/V$. Approximating the sum by an integral is valid as long as the energy separation of typical adjacent states is small compared to τ .

The quantum concentration is the reciprocal of the volume of a cube with sides roughly equal to the de Broglie wavelength at the typical thermal velocity. The ratio n/n_Q gives an estimate of the number of particles occupying a typical one particle quantum state at the given temperature (see below). Provided that n/n_Q is small a gas is in the classical limit and quantum effects are small. An ideal gas is a gas of non-interacting particles in the classical limit. As an example, for He gas at STP $n \simeq 2.69 \times 10^{25} \text{ m}^{-3}$ and $n_Q \simeq 7.83 \times 10^{30} \text{ m}^{-3}$, so that $n/n_Q \simeq 3.4 \times 10^{-6}$ — well in the classical regime.

The average thermal energy of the particle is given by

$$U = \tau^2 \left(\frac{\partial \ln Z_1}{\partial \tau} \right) = \frac{3}{2} \tau = \frac{3}{2} k_B T.$$

The average occupancy of any quantum state obeys the inequality

$$P(\mathbf{n}) = \frac{1}{Z_1} \exp \left(-\frac{\epsilon_{\mathbf{n}}}{\tau} \right) < \frac{1}{Z_1} = \frac{n}{n_Q},$$

so that this is low for most gases at STP. This gives a more precise meaning to the quantum concentration.

3.1 N atoms in a box

If we combine 2 independent systems A and B , then the partition function of the combined system will be

$$Z_{A+B} = \sum_{s_A, s_B} \exp \left(-\frac{\epsilon_A + \epsilon_B}{\tau} \right) = Z_A Z_B.$$

Thus, if we have N non-interacting, distinguishable atoms in a box the partition function will be

$$Z_1 Z_2 \dots Z_N.$$

However, in reality the identical atoms are indistinguishable, so that we must eliminate the terms which represent permutations of the atoms between a single collection of states. This

will reduce the combined partition function by a factor of $N!$. The N single particle partition functions are also identical, so that we get

$$Z_N = \frac{1}{N!} Z_1^N = \frac{(n_Q V)^N}{N!}.$$

This result only applies when $n \ll n_Q$, *i.e.* in the classical regime. Recall that in this state the number of particles occupying a single state is small, so that the quantum corrections which depend on the mean occupancy of a single particle state are negligible.

We can now calculate the mean energy in an N particle ideal gas,

$$U = \tau^2 \left(\frac{\partial \ln Z_N}{\partial \tau} \right)_{N,V} = \frac{3}{2} N \tau,$$

a simple generalization of the result for a single particle. The Helmholtz free energy of the gas is

$$F = -\tau \ln Z_N = -N \tau \ln \left[\left(\frac{M \tau}{2 \pi \hbar^2} \right)^{\frac{3}{2}} V \right] + N \tau \ln N - N \tau,$$

where we have used Stirling's formula. The pressure of the gas is then

$$p = - \left(\frac{\partial F}{\partial V} \right)_{\tau} = \frac{N \tau}{V} = \frac{N k_B T}{V},$$

a very familiar result — the ideal gas law. The entropy is

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V = N \ln \left[\left(\frac{M \tau}{2 \pi \hbar^2} \right)^{\frac{3}{2}} V \right] + \frac{5}{2} N - N \ln N = N \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right],$$

where the concentration (number density) is $n = N/V$. This result is known as the *Sackur-Tetrode equation*.

3.2 Equipartition of energy

The total mean energy

$$U = \frac{3}{2} N \tau$$

can be ascribed to a contribution of $\frac{1}{2} \tau$ from each of the 3 degrees of freedom of the N particles in the system. This arises from a general property of classical statistical mechanical systems.

If a variable, a generalized coordinate or a generalized momentum, appears only quadratically in the Hamiltonian, then it will make a contribution of $\frac{1}{2} \tau$ to the mean total energy of the system. For a classical system

$$Z \propto \int \exp \left(-\frac{H}{\tau} \right) dp_1 \dots dp_N dq_1 \dots dq_N,$$

so that if we can isolate the variable x with $H = H' + ax^2$ and H' independent of x , then the integration over x puts a factor into Z of

$$\zeta = \int_{-\infty}^{\infty} \exp \left(-\frac{ax^2}{\tau} \right) dx = \sqrt{\frac{\pi \tau}{a}}.$$

This adds a term

$$\ln \zeta = \frac{1}{2} \ln \left(\frac{\pi \tau}{a} \right)$$

to $\ln Z$, and hence a term of $\frac{1}{2}\tau$ to the mean energy.

Thus we get extra degrees of freedom for any generalized coordinate associated with simple harmonic motion. As a result the heat capacity of H_2 goes up in steps as the temperature increases and extra degrees of freedom can be excited.

3.3 Example: entropy of mixing

As discussed earlier, the number of possible arrangements of a mixture of atoms of types A and B is identical to the number of accessible states for the simple binary model, *i.e.* if there are t atoms of type B

$$g(N, t) = \frac{N!}{(N-t)!t!}.$$

The entropy of such a mixture is therefore

$$\begin{aligned}\sigma(N, t) &= \ln g(N, t) \simeq N \ln N - N - (N-t) \ln(N-t) + (N-t) - t \ln t + t \\ &= -(N-t) \ln \left(1 - \frac{t}{N}\right) - t \ln \left(\frac{t}{N}\right) = -N [(1-x) \ln(1-x) + x \ln x],\end{aligned}$$

where we have used Stirling's formula. x is the fraction of atoms of type B . This gives the entropy for the mixing of an alloy, assuming that the atoms intermingle thoroughly.

The question arises in metallurgy, if we melt 2 metals together will they intermingle thoroughly or will they separate into unmixed crystals. The answer depends on the interactions between the atoms in the solid. If the interaction energies are all equal (a very special case), then the free energy does not depend on the make up of the solid and we may write

$$F = F_0 + N\tau [(1-x) \ln(1-x) + x \ln x]$$

for the mixture. The free energy of the same quantity of unmixed metals would be

$$F = (1-x)F_0 + xF_0 = F_0,$$

so that the free energy of the mixture will always be lower in this case.

The entropy increase associated with mixing causes a small amount of mixing between the elements even when there is strong repulsion between the different types of atom. Suppose that the nett repulsion energy is $V > 0$, then when a small quantity of B atoms are present, $x \ll 1$, the total repulsive energy is xNV and the free energy is

$$F \simeq NxV - N\tau x + N\tau x \ln x.$$

This is minimized when

$$\left(\frac{\partial F}{\partial x}\right)_{N,\tau} = 0 = NV + N\tau \ln x,$$

i.e. when

$$x = \exp\left(-\frac{V}{\tau}\right).$$

Although it may be small, we see that there is a finite natural level for impurities in any crystal.

3.4 Example: Energy fluctuations

Chapter 3, problem 4. Consider a system in thermal contact with a reservoir. Show that the mean squared fluctuation in the energy of the system is

$$\langle (\epsilon - U)^2 \rangle = \tau^2 \left(\frac{\partial U}{\partial \tau} \right)_V.$$

First,

$$\langle (\epsilon - U)^2 \rangle = \langle \epsilon^2 - 2\epsilon U + U^2 \rangle = \langle \epsilon^2 \rangle - U^2,$$

so that we need an expression for $\langle \epsilon^2 \rangle$. This is a problem in the use of the partition function Z . We have already shown that

$$U = \langle \epsilon \rangle = \frac{1}{Z} \sum_s \epsilon_s \exp \left(-\frac{\epsilon_s}{\tau} \right) = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right)_V.$$

Differentiating this again with respect to τ gives

$$\begin{aligned} \tau^2 \left(\frac{\partial U}{\partial \tau} \right)_V &= - \left(\frac{1}{Z} \right)^2 \tau^2 \left(\frac{\partial Z}{\partial \tau} \right)_V \sum_s \epsilon_s \exp \left(-\frac{\epsilon_s}{\tau} \right) + \frac{1}{Z} \sum_s \epsilon_s^2 \exp \left(-\frac{\epsilon_s}{\tau} \right) \\ &= -U^2 + \langle \epsilon^2 \rangle, \end{aligned}$$

which proves the result.

Note the implicit assumption of ergodicity.

3.5 Example: Spring

Thermal fluctuations in the length of a spring set a limit to the precision with which we can determine a mass using a spring balance. Determine that limit.

We consider a system which consists of a mass m suspended on a spring with spring constant K :

Ignoring fluctuations for the moment, the mass will cause the spring to be extended by an amount ℓ , where

$$K\ell = mg$$

and g is the acceleration due to gravity. If we consider only vertical displacements of the spring from its equilibrium position, then the system consisting of the spring and mass may be modelled as a one dimensional simple harmonic oscillator. The eigenstates are non-degenerate, and have energies

$$\epsilon_n = n\hbar\omega, \quad \text{where} \quad \omega = \sqrt{\frac{K}{m}},$$

and $n = 0, 1, 2, \dots$

The canonical partition function for the system is therefore

$$Z(\tau) = \sum_{n=0}^{\infty} \exp\left(-\frac{n\hbar\omega}{\tau}\right) = \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{\tau}\right)},$$

and this gives the mean energy of the system as

$$U(\tau) = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau} \right) = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{\tau}\right) - 1} \simeq \tau,$$

in the classical limit, $\hbar\omega \ll \tau$.

The fractional error in the mass due to thermal fluctuations in the length of the spring will be roughly equal to the fractional fluctuation in the length of the spring, *i.e.* $\Delta z/\ell$, where Δz is the rms variation in the length of the spring.

The increase in potential energy due to stretching a spring by x is $Kx^2/2$ and the energy of an oscillating spring is equally divided between its kinetic and potential energies (see the discussion of equipartition above), so that in the classical limit the rms fluctuation in the length of the spring is given by

$$\frac{1}{2}K\Delta z^2 = \frac{1}{2}\tau, \quad i.e. \quad \Delta z = \sqrt{\frac{\tau}{K}}.$$

This makes the fractional error in determining the mass

$$\frac{\Delta m}{m} \simeq \frac{\Delta z}{\ell} = \frac{\sqrt{K\tau}}{mg}.$$

For a spring with $K = 10 \text{ N m}^{-1}$ being used to weigh a mass of $1 \mu\text{g}$ at room temperature, 300 K, in the Earth's gravitational field, this gives

$$\frac{\Delta m}{m} \simeq 0.021.$$

4 Problems, Chapter 3

Numbers 3, 6.