

6. Ideal gases

The Maxwell velocity/momentum distribution of an ideal gas was discussed from a classical perspective in Section 5.5. Here we will expand that discussion to gases consisting of atoms which have *internal electronic* degrees of freedom. Molecular gases, which have rotational and vibrational degrees of freedom, will be treated in the following chapter.

Assume our gas consists of N particles in a volume V so as to have a *number density* $n = N / V$. We then have a characteristic spacing a_0 of our particles that is of order $n^{-1/3}$. On the other hand suppose the interaction potential between the particles in our gas has a characteristic range r_0 . Then classically the system will tend to behave as a collection of independent particles provided $a_0 \gg r_0$, and it is in this limit that we regard the system as an *ideal gas*.

Quantum effects are most important when the density is large enough (and the temperature low enough) that there is a large probability that more than one particle will be “competing” for the same quantum state. Let n_k (not to be confused with n introduced above) be the *occupancy number* of some state ϵ_k with \bar{n}_k its average value. A criteria for classical behavior is then

$$\bar{n}_k \ll 1. \quad (6.1)$$

This condition allows us to ignore wave function symmetry considerations that are associated with particles in the same state.

To better understand this condition we note that atoms in our gas case are typically spread over a totality of $\Delta p \Delta q / 2\pi\hbar$ quasi-classical states. Taking $\Delta q \approx a_0$ and $\Delta p \approx \bar{p}$, with \bar{p} a characteristic thermal momentum, this becomes $\bar{p}a_0 / 2\pi\hbar$. The occupation in any single state would be the reciprocal of this quantity and (6.1) becomes $2\pi\hbar / \bar{p}a_0 = h / \bar{p}a_0 \ll 1$ with $h = 2\pi\hbar$ or

$$a_0 \gg h / \bar{p} = \lambda_{dB}, \quad (6.2)$$

where λ_{dB} is a *thermal deBroglie wavelength*; i.e., atoms must be *widely spaced* relative to their deBroglie wavelengths. Taking the characteristic thermal momentum to be $\bar{p} = \sqrt{2mk_B T}$, and ignoring factors of 2π , we can rewrite (6.2) as

$$k_B T \gg \frac{\hbar^2}{2ma_0^2} \quad (6.3)$$

thereby limiting us to temperatures satisfying this inequality.

Whatever the particle density is, if \bar{n}_k is the average occupancy of the state k then we must have

$$\sum_k \bar{n}_k = N \quad (6.4)$$

where N is the total number of atoms in our gas. Of course the actual n_k values must be integers, since a given state is either occupied or it is not; however average values \bar{n}_k can be non-integer.

6.1. The Boltzmann probability from the Gibbs probability

We now derive a form for the Gibbs probability function in the limit $\bar{n}_k \ll 1$; the function obtained in this limit is called the Boltzmann probability. We will do this separately for both the petit and the grand Gibbs ensembles. In both cases we must formally work with “many body” energies.

For the petit case, and in our limit of non-interacting particles, we can treat each particle in translational state k as a *separate sub system*. The many-body energies, E_n , are then the same as the single particle energies, i.e., $E_n \rightarrow \epsilon_k$, which allows us to directly identify $\bar{n}_k = w(\epsilon_k) \equiv w_k$. The probability that this state is occupied is then (see (5.28))

$$\bar{n}_k = a e^{-\beta \epsilon_k}, \quad (6.5)$$

where the normalization constant a is fixed by Eq. (6.4). For our free particles $\epsilon_k = \hbar^2 k^2 / 2m$ where m is the particle mass.

In the grand ensemble our sub systems, which we took to contain one particle in obtaining the petit ensemble, can now contain different numbers of particles and the “many body

energies”, E_n , become $n_k \epsilon_k$; we can then write $w_{nN} \rightarrow w_{n_k}$ which has the form (see Eq. (5.23))

$$w_{n_k} = e^{\beta(\Omega + n_k(\mu - \epsilon_k))} \quad (6.6)$$

where the normalization is fixed by Ω . For large β we can confine ourselves to the lowest “particle numbers” $n_k = 0, 1, 2, \dots$ with the result that w_{n_k} takes on the successive values

$$w_0 = e^{\beta\Omega}, \quad w_1 = e^{\beta(\Omega + (\mu - \epsilon_k))}, \quad w_2 = e^{\beta(\Omega + 2(\mu - \epsilon_k))}, \quad \dots \quad (6.7a,b,c)$$

We now apply the normalization condition (see Eq. (5.5))

$$\begin{aligned} \sum_{n_k} w_{n_k, \epsilon_k} &= 1 \\ &= w_0 + w_1 + \dots \end{aligned} \quad (6.8)$$

where $1 \gg w_1 \gg w_2$ etc. The mean value of n_k is defined by

$$\bar{n}_k = \sum_{n_k} n_k w_{n_k} = 0 \cdot w_0 + 1 \cdot w_1 + \dots \quad (6.9)$$

If multiple particles in the same state are to be avoided, the series must be terminated at w_1 which restricts us to high temperatures; we can then approximate $w_0 = e^{\beta\Omega} \cong 1$, and taking w_1 from Eq. (6.7b) we obtain \bar{n}_k as

$$\bar{n}_k = e^{\beta(\mu - \epsilon_k)}. \quad (6.10)$$

This is called the *Boltzmann occupation* probability. Comparing with (6.5) we see that the normalization constant in that equation is $a = e^{-\beta\mu}$.

6.2. The classical Boltzmann distribution for the ideal gas

Using the Boltzmann occupation probability we can now calculate the average value of some function that depends on \bar{n}_k . For the noninteracting particles of an ideal gas the integral associated with such an average will factor into a *product identical integrals*, one for each particle. In calculating such averages we will work in the quasiclassical limit where we write

$$\sum_k \rightarrow \int \frac{d^3p d^3q}{(2\pi\hbar)^3} \quad (6.11)$$

for the integration associated with each particle where the occupation probability for each particle is now written as

$$\bar{n}_k \rightarrow n(\mathbf{p}, \mathbf{q}; T) = e^{\beta(\mu - (p_x^2 + p_y^2 + p_z^2)/2m - u(x, y, z))} \quad (6.12)$$

where $u(x, y, z)$ is an external potential (e.g. gravity) that acts on the individual particles.

The integrations associated with the individual particles further separate into the product of an integral in momentum space and one in real space; if no external potential is present, the integral involving d^3q simply gives the volume, V . In this case, rather than normalizing each particle to unity, we will normalize to N , the total particle number; i.e., we write

$$\int \frac{d^3p d^3q}{(2\pi\hbar)^3} n(\mathbf{p}, \mathbf{q}; T) = V \int \frac{d^3p}{(2\pi\hbar)^3} e^{\beta(\mu - (p_x^2 + p_y^2 + p_z^2)/2m)} = N. \quad (6.13)$$

This integration fixes the chemical potential, μ .

6.2.1. Momentum distribution in an ideal gas

Carrying out the integration and eliminating μ (see problem 6.1) we can then introduce a differential, $dN_{\mathbf{p}}$, that measures the number of particles per unit volume in the momentum interval d^3p as

$$dN_{\mathbf{p}} = \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z \quad (6.14)$$

where $\int dN_{\mathbf{p}} = N / V$. The corresponding expression in velocity space is

$$dN_{\mathbf{v}} = \frac{N}{V} \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad (6.15)$$

with $\int dN_{\mathbf{v}} = N / V$.

6.2.2. The law of atmospheres

Suppose an external potential $u(x, y, z)$ is present. Rather than a constant density $n = N/V$ we now have $n = n(x, y, z)$ and the number of particles $dN_{\mathbf{r}}$ in a volume element $dx dy dz$ can be written $dN_{\mathbf{r}} = n(\mathbf{r}) d^3r$. One well known case corresponds to the density of the earth's atmosphere with respect to various molecules. Here we limit to the case of a single specie

with mass m corresponding to a potential $u(z) = mgz$ with z measured from the earth's surface. To calculate the effect of this potential we write $\epsilon = p^2 / 2m - mgz$ in place of the kinetic energy in Eq. (6.13). The result of such a calculation is

$$n(z) = n(z=0)e^{-\beta mgz} \quad (6.16)$$

An obvious consequence of Eq. (6.16) is that molecules with different masses have different concentrations as the altitude increases, heavier ones tending to lie lower.

6.3. The free energy of an ideal gas

We recall our earlier equation (5.14) for the free energy

$$F = -\frac{1}{\beta} \ln \left(\sum_n e^{-\beta E_n} \right). \quad (6.17)$$

In our ideal gas the energy levels of an N -particle gas as a whole have the form $E_n = \epsilon_1 + \epsilon_2 \cdots \epsilon_N$ where in the absence of any constraints the individual ϵ_i in this sum can take on any of their allowed values so long as their sum is equal to E_n . Since we are summing over *all values of n* we can write the sum in Eq. (6.17) as

$$\begin{aligned} \sum_n e^{-\beta E_n} &= \sum_{k_1} \sum_{k_2} \cdots \sum_{k_N} e^{-\beta(\epsilon_{k_1} + \epsilon_{k_2} \cdots \epsilon_{k_N})} \\ &= \left(\sum_k e^{-\beta \epsilon_k} \right)^N. \end{aligned} \quad (6.18)$$

In doing so we will encounter terms where two or more particles are in the same state but as discussed in Section 6.1 at high temperatures multiple occupancy of states is rare¹, so for the classical case we can safely ignore such terms and use (6.18) as it is. However we still need to modify it to account for the fact that identical quantum particles are indistinguishable. As discussed in Subsection 5.4.2 (see Eq. (5.42)) we must therefore divide the summation by the $N!$ permutations of the particles, in which case (6.18) becomes

$$\sum_n e^{-\beta E_n} = \frac{1}{N!} \left(\sum_k e^{-\beta \epsilon_k} \right)^N \quad (6.19)$$

with the corresponding free energy given by

$$F = -\frac{N}{\beta} \ln \left(\sum_k e^{-\beta \epsilon_k} \right) + \frac{1}{\beta} \ln N!.$$

¹ We emphasize that Eq. (6.18) fails at low temperatures as will be discussed in Chapter 9.

Using Stirling's approximation $\ln N! \cong N \ln N - N = N \ln(N/e)$ we can rewrite this expression as

$$F = -\frac{N}{\beta} \ln \left(\frac{e}{N} \sum_k e^{-\beta \epsilon_k} \right). \quad (6.20)$$

For point-like particles where only quasi-classical degrees of freedom are present (6.20) takes the form

$$F = -\frac{N}{\beta} \ln \left(\frac{e}{N} \int \frac{d^3 p d^3 q}{(2\pi\hbar)^3} e^{-\beta \epsilon(\mathbf{p}, \mathbf{q})} \right). \quad (6.21)$$

6.4. The free energy of an ideal gas with internal degrees of freedom

We now evaluate the free energy of the classical ideal gas for the case where there are *internal degrees of freedom*. We will limit to the case of a single particle specie² and write the total energy of each particle as

$$\epsilon_{\text{tot}} = \epsilon_{\mathbf{p}} + \epsilon_{\text{int}} \quad (6.22)$$

where $\epsilon_{\mathbf{p}}$ is the translational kinetic energy given by

$$\epsilon_{\mathbf{p}} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \quad (6.23)$$

with m the particle mass, and

$$\epsilon_{\text{int}} = \sum_k \epsilon_k \quad (6.24)$$

is the internal energy associated with rotational, vibrational and electronic degrees of freedom of the particle, which we take as discrete, collectively number by k , and denote as ϵ_k . Inserting (6.22) in (6.20) and separating the discrete and continuous contributions we have

$$F = -\frac{N}{\beta} \ln \left(\frac{e}{N} \int \frac{d^3 p d^3 q}{(2\pi\hbar)^3} e^{-\frac{\beta}{2m} (p_x^2 + p_y^2 + p_z^2)} \sum_k e^{-\beta \epsilon_k} \right) \quad (6.25)$$

Carrying out the integrations we can write this as

$$F = -\frac{N}{\beta} \ln \left(\frac{eV}{N} \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} \sum_k e^{-\beta \epsilon_k} \right). \quad (6.26)$$

We can rewrite (6.26) in the form

² The case where two species are present will be discussed in Chapter 11.

$$F = -\frac{N}{\beta} \ln \frac{eV}{N} + Nf(T) \quad (6.27)$$

where the volume only enters the first term and we introduced the strictly temperature dependent function

$$f(T) = -\frac{1}{\beta} \ln \left[\left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} \sum_k e^{-\beta\epsilon_k} \right]; \quad (6.28a)$$

for later use we also give

$$\frac{df}{dT} = \frac{f}{T} - \frac{3}{2}k_B - k_B \frac{\sum_k (\epsilon_k / k_B T) e^{-\epsilon_k / k_B T}}{\sum_k e^{-\epsilon_k / k_B T}}. \quad (6.28b)$$

6.4.1. The equation of state of an ideal gas

We now introduce the *equation of state* which relates P , V , and T . From Eq. (4.31b) we have $P = -(\partial F / \partial V)_T$, and recalling that the volume enters only the first term in (6.27), we get $P = N / V\beta$ or

$$PV = Nk_B T; \quad (6.29)$$

this relation is called the *perfect gas law*. Note it holds even when the particles have internal degrees of freedom which will generally be excited at finite temperatures.

With (6.29) we can construct the Gibbs thermodynamic potential $\Phi = F + PV$ which from (6.27) we can write in terms of T and P as

$$\Phi = -Nk_B T \ln P + N\chi(T) \quad (6.30a)$$

where

$$\chi(T) = f(T) - k_B T \ln k_B T \quad (6.30b)$$

is another strictly temperature dependent function.

6.4.2. The entropy, energy and enthalpy

The thermodynamic expression for the entropy in terms of the free energy was given earlier by Eq. (4.31a) as $S = -(\partial F / \partial T)_V$. Differentiating (6.27) then gives

$$S(V, T) = Nk_B \ln \frac{eV}{N} - N \frac{df(T)}{dT}. \quad (6.31)$$

Using Eq. (6.29) we can rewrite this in terms P and T as

$$S(P, T) = -Nk_B \ln P + Nk_B \ln \frac{e}{\beta} - N \frac{df(T)}{dT}. \quad (6.32)$$

Taking $df(T)/dT$ from (6.28b) we can write the full expression for the entropy as

$$S(V, T) = Nk_B \ln \left[\frac{eV}{N} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\epsilon_k/k_B T} \right] - \frac{3}{2} Nk_B \\ - Nk_B \frac{\sum_k (\epsilon_k / k_B T) e^{-\epsilon_k/k_B T}}{\sum_k e^{-\epsilon_k/k_B T}}. \quad (6.33)$$

The energy follows from the definition $E = F + TS$ which on combining (6.27) and (6.31) gives

$$E = -Nk_B T \ln \frac{eV}{N} + Nf(T) + T \left[Nk_B \ln \frac{eV}{N} - N \frac{df(T)}{dT} \right] \\ = Nf(T) - NT \frac{df(T)}{dT}; \quad (6.34)$$

note that the energy is a function only of the temperature for an ideal gas; in particular it is independent of the volume. Again inserting $f(T)$ and $df(T)/dT$ from (6.28a,b) we have

$$E = \frac{3}{2} Nk_B T + N \frac{\sum_k \epsilon_k e^{-\epsilon_k/k_B T}}{\sum_k e^{-\epsilon_k/k_B T}} \quad (6.35)$$

which is simply the sum of the average translational kinetic energy together with the average of the internal energies calculated in the usual way, and could have been written down directly.

The heat function, $W = E + PV$ follows immediately from (6.34) and (6.29) as

$$W = E + Nk_B T. \quad (6.36)$$

Note F , Φ , S , E and W are not directly measurable and have to be inferred from other quantities like the equation of state and heat capacity; the first of these was given above and we discuss the latter next.

6.4.3. Heat capacities

In section 4.5 we introduced thermodynamic definitions for the heat capacities, $C_V = (\partial E / \partial T)_V$, given by Eq. (4.19), and $C_P = (\partial W / \partial T)_P$, which follows on combining (4.21) and (4.23). Using Eq. (6.35) we can now write the constant volume heat capacity as

$$\begin{aligned}
C_V &= \frac{dE}{dT} = \frac{d}{dT} \left(\frac{3}{2} N k_B T + N \frac{\sum_k \epsilon_k e^{-\epsilon_k / k_B T}}{\sum_k e^{-\epsilon_k / k_B T}} \right) \\
&= \frac{3}{2} N k_B + N k_B \frac{\sum_k (\epsilon_k / k_B T)^2 e^{-\epsilon_k / k_B T}}{\sum_k e^{-\epsilon_k / k_B T}} - N k_B \frac{\left(\sum_k (\epsilon_k / k_B T) e^{-\epsilon_k / k_B T} \right)^2}{\left(\sum_k e^{-\epsilon_k / k_B T} \right)^2}
\end{aligned} \tag{6.37a}$$

Eq. (6.36) can be rewritten in the more compact form as

$$C_V = \frac{3}{2} N k_B + N k_B \overline{\left(\frac{\epsilon_k}{k_B T} \right)^2} - N k_B \overline{\left(\frac{\epsilon_k}{k_B T} \right)}^2. \tag{6.37b}$$

From (4.21b) we have $C_P = (\partial W / \partial T)_P$ and using (6.36) for W we obtain the constant pressure heat capacity as

$$C_P = C_V + N k_B. \tag{6.38}$$

As discussed in Section 4.8 we can introduce specific quantities in which we normalize with respect to the particle number, N . Hence we also define the heat capacities per particle as³

$$c_P = C_P / N \quad \text{and} \quad c_V = C_V / N. \tag{6.39a,b}$$

According to equations (6.37) and (6.38), in the absence of internal degrees of freedom (those associated with the energy levels ϵ_k), the specific constant volume and constant pressure heat capacities would be

$$c_V = \frac{3}{2} k_B \quad \text{and} \quad c_P = \frac{5}{2} k_B. \tag{6.40a,b}$$

In the next chapter we will discuss additional contributions arising from rotational and vibrational degrees of freedom in molecular ideal gases.

In practice one can often regard the heat capacity as *nearly constant* over some range of temperatures and we will now develop expressions for the thermodynamic potentials in terms of a constant c_V , and in particular the contribution in excess of that given by (6.40a,b). From Eq. (6.34) the heat capacity can be written in terms of the function $f(T)$ in Eq. (6.28a,b) as

³ It is also common to normalize quantities with respect to the volume as opposed to the particle number.

$$c_V = \frac{d}{dT} \left(f(T) - T \frac{df(T)}{dT} \right) = -T \frac{d^2 f(T)}{dT^2}. \quad (6.41)$$

With our assumption that c_V is constant, we can directly integrate twice to obtain

$$f(T) = -c_V T \ln T - \zeta k_B T + \epsilon_0 \quad (6.42)$$

where ϵ_0 and ζ are constants of integration; ϵ_0 represents an overall constant shift of the energy and can be set to zero whereas ζ is called the *chemical constant*⁴. Referring to Eq. (6.27) we can now write the free energy as

$$F(V, T) = N\epsilon_0 - Nk_B T \ln \frac{eV}{N} - Nc_V T \ln(k_B T) - N\zeta k_B T. \quad (6.43)$$

The energy follows directly from integrating $c_V = dE / dT$ as

$$E = N\epsilon_0 + Nc_V T, \quad (6.44)$$

where again we can choose $\epsilon_0 = 0$. The Gibbs free energy is defined as (see Eq. (4.25b)) $\Phi = F + PV$ and combining (6.43) and the equation of state $PV = Nk_B T$ (see (6.29)) we can write Φ as

$$\Phi(V, T) = N\epsilon_0 - Nk_B T \ln \frac{eV}{N} - Nc_V T \ln(k_B T) - N\zeta k_B T + Nk_B T.$$

To rewrite Φ in terms of its natural variables we replace V using the equation of state and note that $c_P = c_V + k_B$ obtaining

$$\Phi(P, T) = N\epsilon_0 + Nk_B T \ln P - Nc_P T \ln(k_B T) - N\zeta k_B T. \quad (6.45)$$

Similarly

$$W = N\epsilon_0 + Nc_P T. \quad (6.46)$$

The entropy follows from Eq. (4.31a), $S = (-\partial F / \partial T)_V$, as

$$S(V, T) = Nk_B \ln \frac{eV}{N} + Nc_V \ln(k_B T) + N(c_V + \zeta k_B), \quad (6.47a)$$

or from (4.32a), $S = (-\partial \Phi / \partial T)_P$, as

$$S(P, T) = -Nk_B T \ln P + Nc_P \ln(k_B T) + N(c_P + \zeta k_B). \quad (6.47b)$$

6.5. Adiabatic processes

⁴ The chemical constant, ζ , can be thought of as a kind of temperature independent internal entropy about which we will comment further on in section 6.8.

We now consider changes in which the entropy remains constant but the temperature and volume or equivalently the temperature and pressure change. Such processes were earlier termed adiabatic. An example of such a processes is the passage of a sound wave in which the velocity and density oscillate $\pi / 2$ out of phase at some point fixed in space, but with minimal transfer of heat between the temperature maxima and minima. Holding the entropy constant in Eq.'s (6.47a,b) we obtain the two separate equations

$$V^{k_B} T^{c_V} = \text{const.} \quad \text{and} \quad P^{-k_B} T^{c_P} = \text{const.}$$

Rearranging

$$V^{k_B/c_V} T = \text{const.} \quad \text{and} \quad P^{-k_B/c_P} T = \text{const.} \quad (6.48)$$

and taking the ratio we obtain

$$P V^{c_P/c_V} = P V^\gamma = \text{const.}; \quad \gamma \equiv c_P / c_V. \quad (6.49)$$

6.6. Perfect monatomic gas

Even a monatomic gas has internal degrees of freedom. To incorporate them we return to Eq. (6.26) and rewrite it as

$$F = -\frac{N}{\beta} \ln \left(\frac{eV}{N} \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} Z_{\text{total}} \right) \quad (6.50)$$

where

$$Z_{\text{total}} = \sum_k e^{-\beta\epsilon_k} \quad (6.51)$$

is the electronic partition function; all levels can be measured from the ground state, ϵ_0 , which we set to zero. The sum here involves all quantum numbers *including* those involving degenerate levels. If degenerate levels are present we can sum strictly over the principle electronic quantum number and incorporate a degeneracy factor in the sum; i.e., we can write (6.51) in the form

$$Z_{\text{total}} \rightarrow \sum_k g_k e^{-\beta\epsilon_k} \quad (6.52)$$

Atoms usually ionize before undergoing excitation to higher lying principal electronic levels, so in practice the most important electronic levels are low lying ones involving the electron spin, S , the electron orbital, L , and the nuclear, I , angular momentum quantum numbers. If we ignore spin-orbit and hyperfine interactions and set $\epsilon_0 = 0$ then this would lead to ground

state degeneracies of $g_S = 2S + 1$, $g_L = 2L + 1$ and $g_I = (2I + 1)$. Comparing Eq. (6.50) with (6.43) and incorporating the factor $(m / 2\pi\hbar^2)^{3/2}$ as a translational chemical constant, ζ_{trans} , we can then identify the following four contributions to the overall chemical constant ζ :

$$\zeta_{\text{trans}} = \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right); \quad \zeta_S = \ln(2S + 1); \quad \zeta_L = \ln(2L + 1); \quad \zeta_I = \ln(2I + 1) \quad (6.53)$$

together with a translational specific heat $c_V = 3k_B T / 2$. In the presence of a large spin orbit splitting, $\Delta\epsilon_{SO}$, and where $k_B T \ll \Delta\epsilon_{SO}$ the combined chemical constant rather than being given by $\zeta_L + \zeta_S = \ln[(2S + 1)(2L + 1)]$ would be replaced by

$$\zeta_J = \ln(2J + 1) \quad (6.54)$$

where J is the total angular momentum of the ground state.

Note that the last three terms in the chemical constant in Eq. (6.53) are equivalent to a *temperature independent* entropy term in the free energy in that they involve energy levels that are fully occupied, independent of temperature. In most systems splittings between these levels are present, those involving the nuclear spin I being the smallest, so that as the temperature approaches zero the occupation higher energy levels would go to zero; i.e., this entropy ultimately “freezes out” at low sufficiently low temperatures. But as the associated energy splittings become comparable to $k_B T$ they result in temperature-dependent contributions to the heat capacity which require a case by case (and possibly a numerical) treatment. This is discussed further in the next section.

6.7. The third law of thermodynamics and residual entropy

Experimentally it is well established the change in entropy, ΔS , associated with a change in temperature, ΔT , approaches zero as the absolute temperature approaches zero,

$$\left(\frac{dS}{dT} \right)_{T \rightarrow 0} \rightarrow 0. \quad (6.55)$$

It then follows that the heat capacity also goes to zero. This is the so-called *third law of thermodynamics*, also called Nernst’s law (1906).

This property of S follows quite naturally from quantum statistics. As the temperature falls toward absolute zero, and the kinetic energy associated with translational motion falls, interactions between particles generally results in a “condensation”, from the gaseous phase

considered above⁵, into some form of liquid⁶ or solid system. For solids the free motion of the particles is then replaced by the normal mode harmonic oscillations about their equilibrium positions, the entropy of which goes to zero with temperature. We are then left with various internal degrees of freedom of our particles, such as the atomic angular momentum values considered in the previous subsection⁷. For simplicity we here limit ourselves to those associated with the quantum number J . If we have $k_B T \gg \Delta E(J)$ where $\Delta E(J)$ is a fine-structure splitting, the added entropy following from this degree of freedom (see (6.47)) will be

$$\begin{aligned} S_{\text{residual}} &= N k_B \zeta_J \\ &= N k_B \ln(2J+1) \end{aligned} \tag{6.56}$$

and, in the temperature range considered, independent of temperature, although nonzero; the associated heat capacity will nearly vanish and one might conclude that Nernst's law is satisfied.

As the temperature continues to fall and we enter a regime where $k_B T \approx \Delta E(J)$ the occupation of the various fine structure sub levels will be governed by a temperature dependent partition function, $Z_J(T)$, and S again becomes temperature dependent. Finally we will enter a regime where $k_B T \ll \Delta E(J)$. Then $Z_J(T) \rightarrow 1$ and the entropy contributed by these levels goes to zero as $\exp(-\Delta E / k_B T)$ where ΔE is the splitting between the first excited state and the ground state and Nernst's law is satisfied asymptotically. One then says that the manifold of fine-structure split levels has “frozen out”. At temperatures approximately 10^{-3} times lower the $(2I+1)$ nuclear spin levels would similarly freeze out.

This suggests that the entropy associated with all degrees of freedom might go to zero as T approaches zero. If the system was in global equilibrium this is presumed to be the case. However in solids certain defects or irregularities are generally present.⁸ This produces a so-called residual, or frozen-in entropy associated with all the different configurations such defects could display. The associated energy barriers for the system to release these defects are large and

⁵ An exception is a meta-stable dilute gas of atoms bound by an external magnetic or optical potential.

⁶ Systems that are liquid at the very lowest temperatures include the two isotopes of helium and a gravitationally bound neutron star.

⁷ In forming chemical bonds in the solid phase the orbital and spin quantum numbers of the outer “valence electrons” of the atoms are folded into indices associated with the various Bloch energy bands. However f electrons in rare earth based materials retain some of their atomic character since their orbitals fall largely inside those of the valence electrons.

⁸ Such defects include atoms occupying interstitial positions in a background lattice or vacancies in which an atom is missing from a lattice site.

the time times for this to happen become prohibitively long. A famous example is that of ice where each water molecule can take on multiple orientations within the lattice. In quantum mechanical liquids the entropy can indeed go to zero.

Appendix 6A. The Maxwell - Boltzmann distribution from the maximum entropy principle

At the beginning of Chapter 4 we noted that in all processes involving macroscopic matter the entropy increases or, in the limit of an ideally reversible process, remains constant. Here we will use this experimentally observed property to derive the Maxwell-Boltzmann distribution function. This approach differs from that used in Section 3.4 which argued the form of the distribution function from the statistical independence of the subsystem probabilities, and hence their multiplicative behavior, together with the property that the subsystem energies were additive.

We earlier introduced a dimensionless entropy as⁹ $\sigma^{(a)} = \ln \Delta\Gamma^{(a)}$ (see Eq. (3.19)) where $\Delta\Gamma^{(a)}$ is an effective interval of quantum numbers associated with the occupied energy levels of the a^{th} subsystem having an energy $\bar{E}^{(a)}$. To make this statement more precise, suppose the number of states available to the a^{th} subsystem is $G^{(a)}$. We further suppose that these states are to be occupied by $N^{(a)}$ particles. We identify the effective interval in quantum number space, $\Delta\Gamma^{(a)}$, as the number of ways these particles can be accommodated in these $G^{(a)}$ states assuming them to be indistinguishable, but without regard to multiple occupancy. With the latter restriction each particle can go in any of the $G^{(a)}$ states; i.e., there are $G^{(a)}$ states available to the first particle, $G^{(a)}$ available to the second and so on to accommodate all $N^{(a)}$ particles for a total of $(G^{(a)})^{N^{(a)}}$ different many body states. Dividing by $N^{(a)}!$ to account for the indistinguishability of these particles we then obtain the total width in quantum number space, $\Delta\Gamma^{(a)}$, as

$$\Delta\Gamma^{(a)} = \frac{(G^{(a)})^{N^{(a)}}}{N^{(a)}!}. \quad (6A.1)$$

The total width over all sub systems is then

⁹ It can also be written $\sigma^{(a)} = -\ln w^{(a)}(\bar{E})$ through Eq. (3.17).

$$\Delta\Gamma = \prod_a \Delta\Gamma^{(a)} . \quad (6A.2)$$

In equilibrium the (dimensionless) total entropy,

$$\ln \Delta\Gamma = \sum_a \ln \Delta\Gamma^{(a)} , \quad (6A.3)$$

is maximal and therefore we maximize (6A.3) with respect to the occupancy, $N^{(a)}$.

To obtain a non trivial result we must subject the maximization to the constraints imposed by fixing the total particle number, N_0 ,

$$N = \sum_a N^{(a)} = N_0 \quad (6A.4)$$

and the total energy

$$E = \sum_a N^{(a)} E^{(a)} = E_0 \quad (6A.5)$$

where N_0 and E_0 are the constrained values of these variables; this is done using Lagrange's method of undetermined multipliers according to the following prescription¹⁰

$$\frac{d \ln \Delta\Gamma}{dN^{(a)}} + \alpha \frac{dN}{dN^{(a)}} + \beta \frac{dE}{dN^{(a)}} = 0 . \quad (6A.6)$$

Inserting (6A.3), (6A.4) and (6A.5) into (6A.6) gives

$$\frac{d}{dN^{(a)}} \sum_a \left(\ln \Delta\Gamma^{(a)} + \alpha N^{(a)} + \beta N^{(a)} E^{(a)} \right) = 0 \quad (6A.7)$$

and using (6A.1) we have

$$\frac{d}{dN^{(a)}} \sum_a \left(N^{(a)} \ln G^{(a)} - \ln(N^{(a)}!) + \alpha N^{(a)} + \beta N^{(a)} E^{(a)} \right) = 0 . \quad (6A.8)$$

Introducing the Sterling approximation, $\ln(N^{(a)}!) \cong N^{(a)} \ln N^{(a)} - N^{(a)}$, and carrying out the differentiation gives

$$\ln G^{(a)} - \ln N^{(a)} + \alpha + \beta E^{(a)} = 0 . \quad (6A.9)$$

or

$$N^{(a)} = G^{(a)} e^{-\alpha - \beta E^{(a)}} . \quad (6A.10)$$

¹⁰ Our definition of the multipliers here is chosen to conform with those introduced in our earlier derivation of the distribution function.

As in section 6.1, for a non-interacting gas we can associate the subsystems energies, $E^{(a)}$, with the individual particle states, ϵ_k , and $N^{(a)} / G^{(a)}$ with the occupation numbers, \bar{n}_k , to obtain

$$\bar{n}_k = e^{-\alpha - \beta \epsilon_k} . \quad (6A.11)$$

On writing $a = e^{-\alpha}$ we recover Eq. (6.5).

We note in passing that we can, formally, use the above procedures to calculate the entropy of a system that is not in equilibrium. Here one would assign occupations $N^{(a)}$ to the $G^{(a)}$ states having energies $E^{(a)}$ which also satisfy our constraints, Eq.'s (6A.4) and (6A.5), and then calculate $\ln \Delta \Gamma$.

Problems

- 6.1. Carry out the integral in Eq. (6.13) to obtain an expression for $\mu = \mu(N, V, T)$. What is the value of the chemical potential of the vacuum?
- 6.2. Use Eq.'s (6.31) and (6.32) for the case of no internal degrees of freedom to obtain Eq. (6.49).
- 6.3. You are given a gas of N atoms of mass m in a volume V possessing two internal energy levels: $\epsilon = 0$ and $\epsilon = \Delta \epsilon$. Calculate temperature dependence of F , E , W , P , C_V and C_P . Give the asymptotic forms for these quantities as $k_B T \gg \Delta \epsilon$ and $k_B T \ll \Delta \epsilon$.
- 6.4. Carry out the same calculations as in problem 6.3 but for the case the upper level is doubly degenerate.