Statistical Physics

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4   Ideal gas

We now develop some of the ideas introduced above in the context of an ideal gas, also called a perfect gas.

4.1   Density of states

Recall from the example of Section 1.4 that the stationary states of the free Hamiltonian in a cubic, periodic box could be labelled by wave vectors $\mathbf{k}$ (1.2.3). In the thermodynamic limit (1.2.5) the allowed values of $\mathbf{k}$ become continuous. In this limit we can replace the sum over microstates, which may be difficult to carry out in practice, with an integral over $\mathbf{k}$. In order to make this replacement, we need to know the number of microstates in an infinitesimal range of $\mathbf{k}$, namely the **density of states**.

Consider a fixed range in one direction $(k_x, k_x + \mathrm{d}k_x)$. As L is increased, the number, $\mathrm{d}n_x$, of integers n_x which satisfy

$$\frac{2\pi n_x}{L} \in (k_x, k_x + \mathrm{d}k_x) \tag{4.1.1}$$

also increases. In fact it is $\mathrm{d}n_x = (L/2\pi)\mathrm{d}k_x$. Figure 7 shows how this number increases as L is increased. Thus the number of states in an infinitesimal volume in $k-$space is

$$\mathrm{d}^3 n \;=\; \frac{V}{(2\pi)^3}\,\mathrm{d}^3 k \tag{4.1.2}$$

where the volume $V = L^3$.

The quantum (not thermal) expectation value of some observable $\hat{X}$ is given by the sum over single particle states which we label by $|\mathbf{k}\rangle$

$$\langle \hat{X} \rangle \;=\; \sum_{\mathbf{k}} \langle \mathbf{k}|\hat{X}|\mathbf{k}\rangle \,. \tag{4.1.3}$$

(We will, of course, eventually be interested in thermal expectation values, but this type of sum must be done in that case too.) In the thermodynamic limit the allowed values of $\mathbf{k}$ tend toward a continuum, and over an infinitesimal range of wavevectors observables are nearly constant. Therefore, in this infinitesimal range we can approximate summation over wavevectors by a constant over this range $X(\mathbf{k})$ times the number of states in that range:

$$\sum_{\mathbf{k}'=\mathbf{k}}^{\mathbf{k}+\mathbf{dk}} \langle \mathbf{k}'|\hat{X}|\mathbf{k}'\rangle \;=\; X(\mathbf{k})\,\mathrm{d}^3 n \;=\; \frac{V}{(2\pi)^3}\,X(\mathbf{k})\,\mathrm{d}^3 k \,. \tag{4.1.4}$$

The quantities we will look at depend only on the microstate energies ε, which are functions of $k = |\mathbf{k}|$, or $p = \hbar k$. Therefore, we can perform the angular integral over
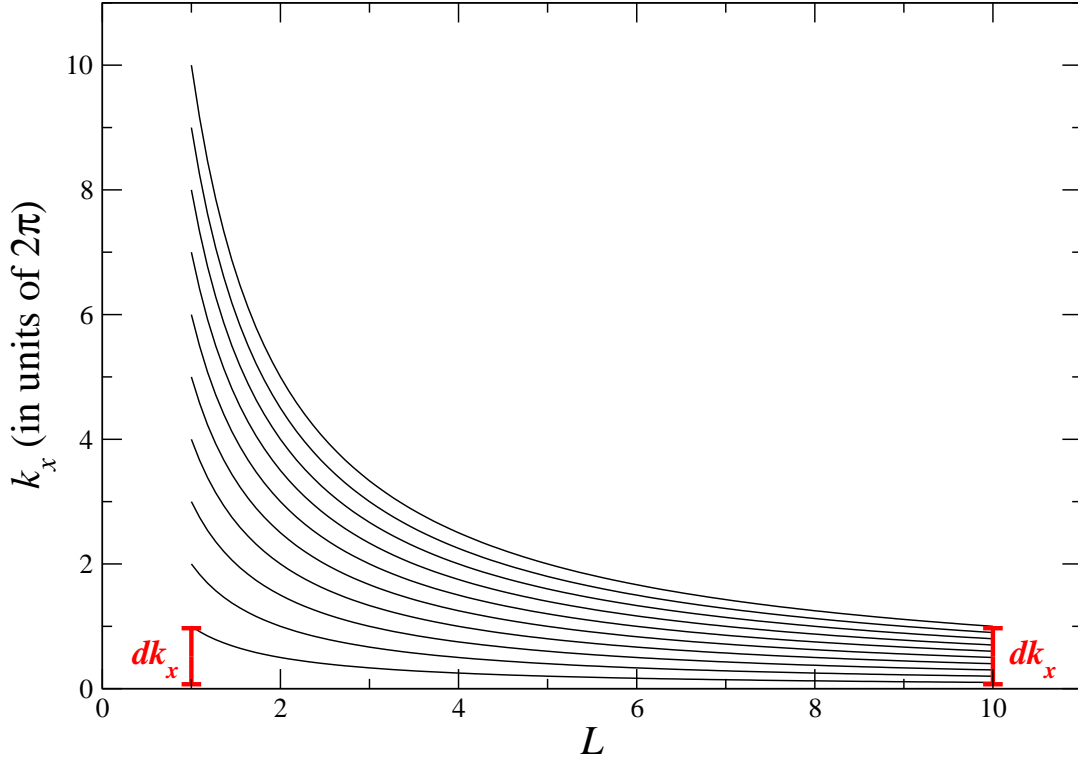
Figure 7: Ten lowest allowed wavenumbers k_x (in units of 2π) in a box with length L in the $x-$direction. The number of states in a range of k_x increases as L increases as $\mathrm{d}n_x = L\,\mathrm{d}k_x/(2\pi)$. In the figure $\mathrm{d}n_x = 1$ at $L = 1$ and $\mathrm{d}n_x = 10$ at $L = 10$.

the direction of $\mathbf{k}$:

$$\langle \hat{X} \rangle = \frac{V}{(2\pi)^3} \int X(\varepsilon(k))\,\mathrm{d}^3k$$

$$= \frac{V}{(2\pi\hbar)^3} \int X(\varepsilon(p))\,4\pi p^2\,\mathrm{d}p \equiv \int X(\varepsilon(p))\,g(p)\,\mathrm{d}p \qquad (4.1.5)$$

$$= \frac{V}{2\pi^2\hbar^3} \int X(\varepsilon)\,p^2\,\frac{\mathrm{d}p}{\mathrm{d}\varepsilon}\,\mathrm{d}\varepsilon \equiv \int X(\varepsilon)\,g(\varepsilon)\,\mathrm{d}\varepsilon\,. \qquad (4.1.6)$$

In the last two lines, we have implicitly defined the density of states in momentum

$$g(p) = \frac{V}{2\pi^2\hbar^3}\,p^2 \qquad (4.1.7)$$

and in energy

$$g(\varepsilon) = \frac{V}{2\pi^2\hbar^3}\,p^2\frac{\mathrm{d}p}{\mathrm{d}\varepsilon}\,. \qquad (4.1.8)$$

The first definition is nice because it is the same for any energy-momentum relation in 3 dimensions. The second definition is useful in practice, as we will see. Note that although we use the same symbol, $g(p)$ and $g(\varepsilon)$ are different functions, related by

$$g(p)\,\mathrm{d}p = g(\varepsilon)\,\mathrm{d}\varepsilon\,. \qquad (4.1.9)$$

Most of the time we will be discussing gases of nonrelativistic particles, for which

$$\varepsilon(p) \;=\; \frac{p^2}{2m}\,. \tag{4.1.10}$$

Then the density of states becomes

$$g(\varepsilon) \;=\; \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}\,. \tag{4.1.11}$$

Including internal degrees-of-freedom increases the density of states due to degeneracies. For example, the degeneracy of massive particles with spin s is $g_s = 2s+1$; g_s unique states can have the same spatial wavefunction $\psi_{\mathbf{k}}(\mathbf{x})$. Therefore, we must multiply the spin-zero density of states (4.1.11) by g_s

$$g(\varepsilon) \;=\; g_s\,\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}\,. \tag{4.1.12}$$

In arbitrary numbers of dimensions, we must generalise the angular integration, obtaining

$$\boxed{g(\varepsilon) \;=\; g_s\,\frac{V S_D}{(2\pi\hbar)^D}\,p^{D-1}\,\frac{\mathrm{d}p}{\mathrm{d}\varepsilon}\,.} \tag{4.1.13}$$

S_D is the surface area of a unit sphere in D dimensions.

On other occasions we might be interested in a gas of relativistic particles, having dispersion relation $\varepsilon(p) = \sqrt{p^2c^2 + m^2c^4}$. If those particles are photons, with $m = 0$ and $g_s = 2$ (photons have no longitudinal polarisation) then

$$g(\varepsilon)\,\mathrm{d}\varepsilon \;=\; V\,\frac{\varepsilon^2\,\mathrm{d}\varepsilon}{\pi^2\hbar^3c^3} \tag{4.1.14}$$

or, writing $\varepsilon = \hbar\omega$,

$$g(\omega)\,\mathrm{d}\omega \;=\; V\,\frac{\omega^2\,\mathrm{d}\omega}{\pi^2c^3}\,. \tag{4.1.15}$$

4.2   Partition function

In order to compute the partition function for an ideal gas, let us first define for a single particle the quantity

$$z \;=\; \sum_{\mathbf{k}} e^{-\beta\varepsilon_{\mathbf{k}}} \tag{4.2.1}$$

$$=\; \int_0^{\infty}\mathrm{d}\varepsilon\,g(\varepsilon)\,e^{-\beta\varepsilon} \tag{4.2.2}$$

$$=\; \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty}\mathrm{d}\varepsilon\,\sqrt{\varepsilon}\,e^{-\beta\varepsilon}\,. \tag{4.2.3}$$

If we substitute $y^2 = \beta\varepsilon$, which implies $\mathrm{d}\varepsilon = 2y\,\mathrm{d}y/\beta$, then

$$z \;=\; \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{\beta^{3/2}}\int_0^{\infty}\mathrm{d}y\,y^2\,e^{-y^2} \tag{4.2.4}$$

The integral can be shown to be equal to $\sqrt{\pi}/4$.[5] Therefore

$$z = V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3} \tag{4.2.5}$$

where the last step defines the **thermal wavelength** (sometimes written λ_T if there are other lambdas in use.)

$$\boxed{\lambda \equiv \sqrt{\frac{2\pi\hbar^2}{mkT}}.} \tag{4.2.6}$$

In Chap. 7 we will see that thermal behaviour is classical as long as the mean interparticle spacing $(V/N)^{1/3}$ is much bigger than λ. In other words, the particles are far enough apart that the wave-like nature of the quantum particles is negligible. Conversely, quantum effects are resolvable when $(V/N)^{1/3}$ comparable to λ. One way to leave the classical regime is to lower the temperature, consequently lengthening λ.

For N independent particles, we take the product

$$Z = z^N. \tag{4.2.7}$$

Let us obtain the average energy from this partition function. Note that (4.2.5) implies

$$z \propto (kT)^{3/2} \tag{4.2.8}$$

which generalises in D dimensions to

$$z \propto (kT)^{D/2}. \tag{4.2.9}$$

Then

$$
\begin{aligned}
E &= -\left.\frac{\partial}{\partial\beta}\log Z\right|_V \\
&= -N\left.\frac{\partial}{\partial\beta}\log z\right|_V \\
&= -N\left.\frac{\partial}{\partial\beta}\left(-\frac{D}{2}\log\beta\right)\right|_V \\
&= \frac{D}{2}NkT.
\end{aligned}
\tag{4.2.10}
$$

The last line derives a principle of classical thermodynamics called the **equipartition of energy**: that the average energy per particle degree-of-freedom is $\frac{1}{2}kT$. (This assumes that the particle energy depends quadratically on that degree-of-freedom. In an ideal gas a particle's energy is entirely kinetic, and varies quadratically in $\dot{x}_i$.)

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[5] Remember the Gaussian integral $I(a) \equiv \int_{-\infty}^{\infty}dx\,\exp(-ax^2) = \sqrt{\pi/a}$. Differentiating both sides of the equality by a and setting $a = 1$ gives us the result we desire times 2 (due to the different lower limit of integration).

From (3.1.9) we saw that $PV = \frac{2}{3}E$ for an ideal gas, therefore we find

$$\boxed{PV = NkT} \tag{4.2.11}$$

which is known as the **ideal gas law**, **Boyle's law**, and the **ideal gas equation of state**. An equation of state gives the behaviour of dependent thermodynamic variables in terms of independent variables.

4.3 Gibbs' paradox

In this section we will see that we need to multiply the right-hand side of (4.2.7) by another $T-$independent factor.

Let us compute the entropy for an ideal gas. From (3.3.4) we can obtain

$$S = -\left.\frac{\partial F}{\partial T}\right|_V = -\left.\frac{\partial}{\partial T}(-kT\log Z)\right|_V. \tag{4.3.1}$$

Inserting $Z = (V/\lambda^3)^N$ we obtain

$$S = Nk\log V - 3Nk\log\lambda + \frac{3}{2}Nk. \tag{4.3.2}$$

In Chapter 3 we showed that the entropy should be extensive. The second and third terms in (4.3.2) are both extensive, scaling like N (or equivalently like V), but the first term scales like $N\log N$.

The problem is that, by taking $Z = z^N$, we treat each particle as distinguishable, saying that there are z^N arrangements of the N particles. This is consistent with ideas of classical physics: if we know all the particles' initial positions and momenta, then we can track them through all future moments (at least in principle). The inconsistency of (4.3.2) with extensivity was known as Gibbs paradox.

The resolution of the paradox comes from realising that we should not treat the particles as distinguishable, as classical mechanics would let us believe we are capable of doing. We must treat the particles as indistinguishable, as quantum mechanics forces us to do. (We will see this more clearly later.) To get rid of the overcounting of (4.2.7), we must divide by the $N!$ indistinguishable permutations

$$Z = \frac{z^N}{N!} \tag{4.3.3}$$

then, using Stirling's formula $\log N! \simeq N\log N - N$, the entropy composed of 3 terms which are properly extensive:

$$\begin{aligned} S &= Nk\log\frac{V}{N} - 3Nk\log\lambda + \frac{5}{2}Nk \\ &= Nk\left(\log\frac{V}{N\lambda^3} + \frac{5}{2}\right). \end{aligned} \tag{4.3.4}$$

The last line combines factors so that the argument of the logarithm is satisfyingly dimensionless.

4.4   Increase of entropy

We now state the **second law of thermodynamics**.[6] For any thermodynamic process, the *total* change in entropy is nonnegative:

$$\Delta S_{\text{total}} \; \geq \; 0\,. \tag{4.4.1}$$

We can decrease the entropy of a part of a system, by removing heat from it, but then we must consider the entropy of the system and the heat sink before applying the 2nd law. For the rest of this section, let us consider systems in isolation.

It is only for idealised processes, which we sometimes consider for illustration, that $\Delta S_{\text{total}} = 0$. For real systems, which always have some loss due to friction, for example, ΔS_{total} is strictly positive. This fact is the reason why **perpetual motion machines** do not exist.

Let us take 2 disconnected systems, each of which is in thermal equilibrium at temperature T. System 1 is composed of an ideal gas of N_1 particles of type 1, in volume V_1, and system 2 is composed of an ideal gas of N_2 particles of type 2, in volume V_2. (This differs from our discussion in sections 3.4 and 3.5 where the particles were all of the same type.) In this disconnected setup the total entropy is just the sum of the individual entropies

$$S_{\text{init}} \; = \; S_1 + S_2 \qquad \text{before mixing} \tag{4.4.2}$$

with each entropy given by (4.3.4), which we rewrite here as

$$
\begin{aligned}
\frac{S_i}{k} \; &= \; N_i \log \frac{V_i}{(\lambda_i(T))^3 N_i} \; + \; \frac{5}{2} N_i \\
&= \; N_i \log \frac{V_i}{N_i} \; + \; N_i \left[\frac{3}{2} \log \left(\frac{m_i kT}{2\pi \hbar^2} \right) \; + \; \frac{5}{2} \right] \\
&= \; N_i \log \frac{V_i}{N_i} \; + \; N_i B_i(T)\,.
\end{aligned}
\tag{4.4.3}
$$

The last line implicitly defines $B_i(T)$ as the quantity in square brackets above; it differs between $\mathcal{S}_1$ and $\mathcal{S}_2$ if $m_1 \neq m_2$.

Now connect the two boxes and let the gases mix. Call the new entropy S_{12}. Since the types of particles are distinguishable, they constitute separately identifiable subsystems, both occupying volume $V_1 + V_2$. The partition function is then

$$Z_{12} \; = \; \frac{z_1^{N_1}}{N_1!} \frac{z_2^{N_2}}{N_2!}\,. \tag{4.4.4}$$

The fact that the denominator is not $(N_1 + N_2)!$ is a consequence of the particle types being distinct. Now the entropy can be calculated using (4.3.1) to be

$$
\begin{aligned}
\frac{S_{12}}{k} \; = \; & N_1 \left[\log \frac{V_1 + V_2}{N_1} \; + \; B_1(T) \right] \\
& + N_2 \left[\log \frac{V_1 + V_2}{N_2} \; + \; B_2(T) \right]\,.
\end{aligned}
\tag{4.4.5}
$$

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[6]An explanation of this law was given by Boltzmann using his kinetic theory, but it lies outside the scope of this course.

Note that this is the sum of the entropies each gas would have if it were alone in volume $V_1 + V_2$, in other words the total entropy is the sum of **partial entropies**. Now let us calculate the **entropy of mixing**

$$\Delta S \; = \; S_{12} - S_1 - S_2 \; = \; N_1 \log \frac{V_1 + V_2}{V_1} \; + \; N_2 \log \frac{V_1 + V_2}{V_2} \; > \; 0 \,. \qquad (4.4.6)$$

The entropy of mixing together two distinguishable gases is always positive.

Now let us switch to imagining the 2 gases are in fact indistinguishable, made up of the same particle type. Then

$$Z_{12} \; = \; \frac{z_{12}^{N_1 + N_2}}{(N_1 + N_2)!} \qquad (4.4.7)$$

and $B_1(T) = B_2(T) = B_{12}(T)$. The entropy of the joined system is

$$\frac{S_{12}}{k} \; = \; (N_1 + N_2) \log \frac{V_1 + V_2}{N_1 + N_2} \; + \; (N_1 + N_2) B_{12}(T) \,. \qquad (4.4.8)$$

The initial entropies are the same as before. The change entropy due to mixing is

$$\begin{aligned}
\Delta S \; &= \; (N_1 + N_2) \log \frac{V_1 + V_2}{N_1 + N_2} \; - \; N_1 \log \frac{V_1}{N_1} \; - \; N_2 \log \frac{V_2}{N_2} \\
&= \; \log \left[\frac{(V_1 + V_2)^{N_1 + N_2}}{V_1^{N_1} V_2^{N_2}} \frac{N_1^{N_1} N_2^{N_2}}{(N_1 + N_2)^{N_1 + N_2}} \right] \; \geq \; 0 \,. \qquad (4.4.9)
\end{aligned}$$

Even with just one type of particle, the entropy of mixing is positive unless $N_2 = r N_1$ and $V_2 = r V_1$ for constant r. In this case, the densities of the 2 initial systems are equal, so the mixing of the 2 systems can be viewed as a rescaling of $\mathcal{S}_1$ by a factor $(1 + r)$.

4.5   A few remarks on entropy

- Entropy is useful in the field of information theory. Entropy is an inverse measure of information, in some sense. If entropy is large, then we have many possible microstates. Forcing a system into a small set of microstates (by gaining knowledge in this case) then entropy decreases.

- For 2 separate systems $\mathcal{S}_1$ and $\mathcal{S}_2$, the equilibrium entropies S_1 and S_2 were separate maxima with 4 constraints (on N_1, E_1, N_2 and E_2). After mixing, the final equilibrium is achieved by maximising S_{12} with fewer constraints: 3 constraints for distinguishable types (on N_1, N_2 and $E_1 + E_2$), or 2 constraints for indistinguishable types (on $N_1 + N_2$ and $E_1 + E_2$). An increase in entropy is equivalent to an increase in disorder, corresponding to a removal of constraints.

Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapter 7, Appendix B.

2. L D Landau and E M Lifshitz, *Statistical Physics*, (Pergamon Press, 1980), Chater IV.