10. Ideal gas in the low density limit

Blundell and Blundell chapter 2, Baierlein 5.6

In the last chapter, the calculation of $Z(1)$ for the ideal gas was begun. In this chapter, we finish the calculation and discuss when the semi-classical treatment is valid. The concept of a density of states is also introduced.

10.1 Calculation of $Z(1)$

We first finish the job begun in the last chapter:

$$Z(1) = \pi \int_0^\infty \exp\left(-an^2\right) n^2 dn \quad \text{where} \quad a = \frac{\hbar^2 \pi^2}{2kTML^2}$$

The Gaussian integral that should be familiar is:

$$\int_{-\infty}^\infty \exp(-an^2) dn = \left(\frac{\pi}{a}\right)^{1/2}$$

Thus, we see:

$$Z(1) = -\frac{1}{2}\frac{d}{da}\left(\int_{-\infty}^\infty \exp(-an^2)dn\right) = -\frac{1}{2}\frac{d}{da}\left(\frac{\pi}{a}\right)^{1/2} = \frac{\sqrt{\pi}}{4a^{3/2}}$$

The factor $\frac{1}{2}$ comes from the limit 0 to ∞ in the integral for $Z(1)$. Inserting the expression for a gives:

$$Z(1) = \frac{\pi^{3/2}}{8}\left(\frac{2ML^2}{\beta\hbar^2\pi^2}\right)^{3/2} = V\left(\frac{2\pi MkT}{h^2}\right)^{3/2}$$

where $V = L^3$ is the system volume and $h = 2\pi\hbar$ has been used.

10.2 Density of states

Consider again the approximation of a sum by an integral:

$$\sum_{n_x,n_y,n_z} A(n) \rightarrow \frac{1}{8} \int_0^\infty A(n) 4\pi n^2 dn$$

where $A(n)$ is any function of n. Now change variables to k (see 9.3):

$$n = \frac{L}{\pi} k \quad dn = \frac{L}{\pi} dk$$

and we find:

$$\sum_{n_x,n_y,n_z} A(n) \rightarrow \frac{1}{8} \int A(k) \frac{4\pi L^2 k^2}{\pi^2} \frac{L}{\pi} dk = \int A(k)\Gamma(k)dk$$

where:

$$\Gamma(k)dk = \frac{k^2}{2\pi^2} V dk$$

is the number of states with k between k and $k + dk$.

> $\Gamma(k)$ is known as the "density of states" (here, in k space).

Similarly, we can change variables to ϵ:

$$\epsilon = \frac{\hbar^2 k^2}{2M} \Rightarrow \quad k = \left(\frac{2M\epsilon}{\hbar^2}\right)^{1/2} \Rightarrow \quad dk = \frac{dk}{d\epsilon} d\epsilon = \frac{1}{2}\left(\frac{2M}{\hbar^2}\right)^{1/2} \epsilon^{-1/2} d\epsilon$$

Now, to obtain the density of states in energy space, denoted here by $g(\epsilon)$, equate:

$$\Gamma(k)dk = g(\epsilon)d\epsilon$$

and change variables:

$$g(\epsilon)d\epsilon = \left(\frac{2M}{\hbar^2}\right)^{3/2} \frac{V}{4\pi^2} \epsilon^{1/2} d\epsilon$$

The meaning of the density of states $g(\epsilon)$ is that $g(\epsilon)d\epsilon$ is the number of states with energy between ϵ and $\epsilon + d\epsilon$.

If you're unsure of this change of variables from $\Gamma(k)$ to $g(\epsilon)$, you can carry it out as follows: Consider for any function $A(k)$:

$$\int A(k)\Gamma(k)dk = \int A(k)\Gamma(k)\frac{dk}{d\epsilon}d\epsilon = \int A(\epsilon)g(\epsilon)d\epsilon$$

Using the density of states, one can write, for example:

$$Z(1) = \int_0^\infty g(\epsilon)\exp(-\beta\epsilon)d\epsilon$$

Notice that the density of states increases with energy, meaning that at higher energies, more states are available to the particle.
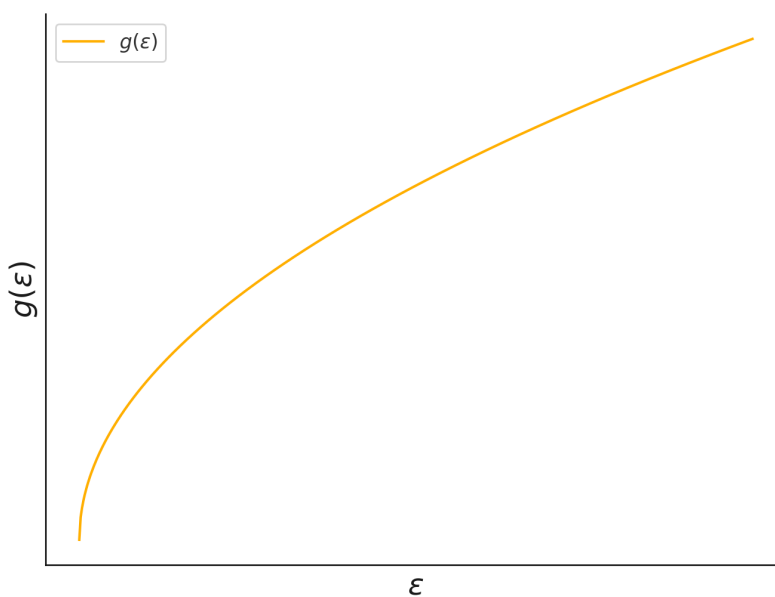

Figure 1: Density of states as a function of energy

10.3 Thermodynamic variables

In the semi-classical treatment developed over this and the previous chapter:

$$Z = \frac{Z(1)^N}{N!} = \frac{V^N}{N!}\left(\frac{2\pi MkT}{h^2}\right)^{3N/2}$$

We now proceed to calculate the usual thermodynamic variables:

$$F = -kT \ln Z = NkT \left[\ln \left(\frac{N}{V} \right) - 1 - \frac{3}{2} \ln \left(\frac{2\pi MkT}{h^2} \right) \right]$$

where Stirling's approximation for $\ln N!$ was used.

Energy:

$$\overline{E} = kT^2 \frac{\partial \ln Z}{\partial T} = \frac{3}{2} NkT$$

Entropy:

$$S = \frac{\overline{E} - F}{T} = Nk \left[\ln \left(\frac{V}{N} \left(\frac{2\pi MkT}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

Pressure:

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{NkT}{V} \quad \text{(ideal gas equation of state)}$$

Heat capacity:

$$C_V = \frac{3}{2} Nk \quad \text{(equipartition)}$$

Note that

- the ideal gas law and equipartition of energy are recovered.

- The recovery of the ideal gas law finally identifies our statistical mechanical definition of temperature (see key point 9) with the thermodynamic temperature.

10.4 Validity of semi-classical treatment

The semi-classical treatment developed here is valid when d_{typ} the typical distance between particles is much larger than the typical thermal de Broglie wavelength λ_{typ}:

$$d_{typ} \gg \lambda_{typ}$$

For an ideal gas, this is equivalent to requiring the number density $\rho = N/V$ be low, specifically:

$$\rho \lambda_{typ}^3 \ll 1$$

Using $\lambda_{typ} = \frac{h}{\sqrt{3MkT}}$, this condition becomes:

$$\rho \left(\frac{h}{\sqrt{3MkT}} \right)^3 \ll 1 \quad \Rightarrow \quad \rho \left(\frac{h^2}{2\pi MkT} \right)^{3/2} \ll 1$$

This inequality is often expressed as $\rho \lambda_{typ}^3 \ll 1$, known as the **classical limit** or **dilute gas limit**. When this condition is violated, quantum effects become important, and we must turn to quantum statistics (Bose-Einstein or Fermi-Dirac statistics).

The semi-classical treatment breaks down when the temperature is very low or the density is very high because, under these conditions, the wavefunctions of individual particles overlap, and quantum indistinguishability becomes essential.
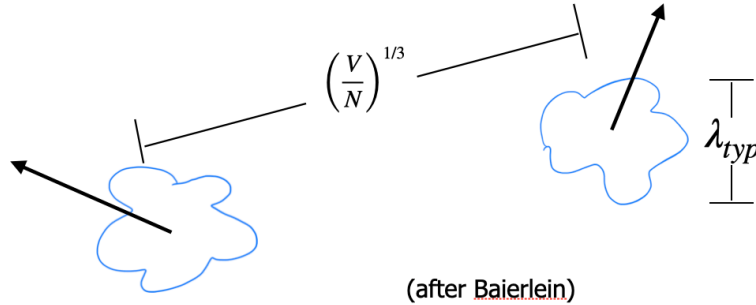

Figure 2: Criterion for assessing validity of semi-classical treatment. Reproduced from Baierlein Fig 5.5

10.5 Summary

In this chapter we completed the calculation of $Z(1)$ for an ideal gas and introduced the concept of a density of states. We discussed the validity of the semi-classical treatment, noting that it is applicable in the low-density limit where the wave packets of individual particles do not overlap. When the typical particle separation becomes comparable to or smaller than the de Broglie wavelength, quantum effects must be considered, and the semi-classical treatment breaks down.

Next we will explore quantum statistics and examine how the behavior of ideal gases changes in the high-density regime where quantum effects become significant.