Weakly Interacting Gas

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1 Introduction to the Weakly Interacting Gas

So far in this course, we have focused on ideal gases—non-interacting gases (up to quantum statistics). Now, we will turn on interactions. This is much more interesting, but also much more difficult. Some of the most important unsolved problems in physics have to do with interactions between a large number of particles.

Our focus here will be on monoatomic gases. We saw that the ideal gas approximation is valid in the dilute limit:

$$\frac{V}{\lambda_Q^3} \gg N \implies \frac{1}{\lambda_Q^3} \gg \frac{N}{V} \tag{1}$$

where N/V is the particle density. Since N/V is small, we can write down a systematic expansion of the equation of state in powers of the density:

$$\frac{P}{k_B T} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \dots \tag{2}$$

The coefficients $B_j(T)$ are called the **virial coefficients**. They encode the macroscopic impact of the microscopic interactions on the equation of state.

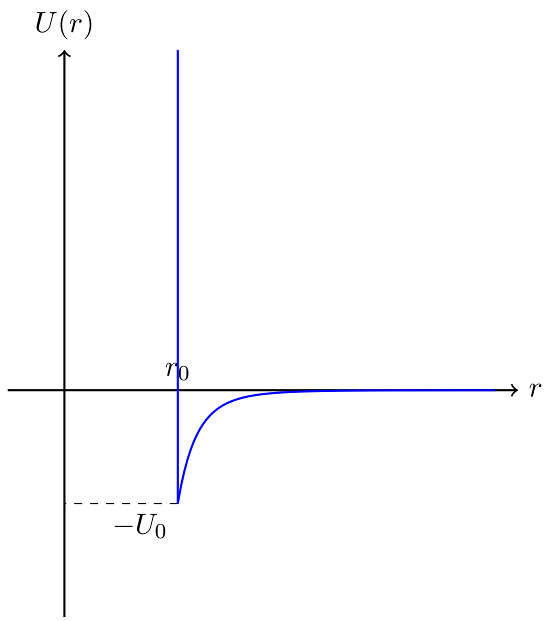
2 Interatomic Potentials

What kind of interactions should we consider?

- A longer-range attractive force, scaling as $1/r^6$, caused by dipole-dipole interactions (the van der Waals interaction).
- A short-range, strong repulsive force, caused by Pauli exclusion and electrostatic repulsion of overlapping electron clouds.

For example, we can model the potential energy $U(r)$ between two atoms using a hard-core repulsion with an attractive tail:

$$U(r) = \begin{cases} \infty & \text{for } r < r_0 \\ -U_0\left(\frac{r_0}{r}\right)^6 & \text{for } r \geq r_0 \end{cases} \tag{3}$$



3 The Partition Function and the Mayer f-function

To find the equation of state, we must evaluate the classical partition function for N identical interacting particles in a volume V:

$$Z_{\text{tot}} = \frac{1}{N!h^{3N}} \int d^{3N}p \int d^{3N}r \exp\left[-\beta \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} U(r_{ij})\right)\right] \tag{4}$$

Because the exponential of a sum is the product of exponentials, we can completely separate the kinetic energy terms (which depend only on momentum) from the potential energy terms (which depend only on position):

$$Z_{\text{tot}} = \frac{1}{N!h^{3N}} \left[\int d^{3N}p \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)\right] \times \left[\int d^{3N}r \exp\left(-\beta \sum_{i<j} U(r_{ij})\right)\right] \tag{5}$$

Step 1: Evaluating the Momentum Integrals

The momentum integral factors into $3N$ identical, independent one-dimensional Gaussian integrals (one for each Cartesian coordinate p_x, p_y, p_z of each of the N particles):

$$\int d^{3N}p \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right) = \left(\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/2m}\right)^{3N} \tag{6}$$

Using the standard Gaussian integral result $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\pi/\alpha}$ where $\alpha = \beta/2m$:

$$\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/2m} = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi m k_B T} \tag{7}$$

Therefore, the total momentum integral evaluates to:

$$\left[\int d^{3N}p \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)\right] = (2\pi m k_B T)^{3N/2} \tag{8}$$

Let us group this result with the $1/h^{3N}$ factor from the density of states. Notice that this recovers the definition of the **thermal de Broglie wavelength**, λ_Q:

$$\frac{1}{h^{3N}}(2\pi m k_B T)^{3N/2} = \left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^{3N} = \frac{1}{\lambda_Q^{3N}} \tag{9}$$

Step 2: Defining the Ideal Gas Partition Function

If the gas were completely non-interacting (an ideal gas), the potential energy would be zero everywhere ($U = 0$). In that case, the spatial integral would simply be the integral of 1 over the volume V for each of the N particles:

$$\int d^{3N}r\,(1) = \left(\int d^3r\right)^N = V^N \tag{10}$$

Combining this with our momentum result yields the classical partition function for an ideal gas:

$$Z_{\text{ideal}} = \frac{1}{N!}\frac{1}{\lambda_Q^{3N}}V^N = \frac{1}{N!}\left(\frac{V}{\lambda_Q^3}\right)^N \tag{11}$$

Step 3: Factoring Z_{ideal} from the Interacting Gas

Returning to our full interacting gas, we can substitute $1/\lambda_Q^{3N}$ back into the equation:

$$Z_{\text{tot}} = \frac{1}{N!}\frac{1}{\lambda_Q^{3N}} \int d^{3N}r \exp\left(-\beta \sum_{i<j} U(r_{ij})\right) \tag{12}$$

To make Z_{ideal} explicitly appear, we multiply and divide the expression by V^N:

$$Z_{\text{tot}} = \left[\frac{1}{N!}\left(\frac{V}{\lambda_Q^3}\right)^N\right] \frac{1}{V^N} \int d^{3N}r \prod_{i<j} e^{-\beta U(r_{ij})} \tag{13}$$

$$Z_{\text{tot}} = Z_{\text{ideal}} \frac{1}{V^N} \int d^{3N}r \prod_{i<j} e^{-\beta U(r_{ij})} \tag{14}$$

This isolates the effect of the interactions entirely within the spatial integral (the configuration integral), scaled by $1/V^N$. We now introduce the **Mayer f-function**, which vanishes when particles are far apart ($U \to 0$):

$$f(r_{ij}) = e^{-\beta U(r_{ij})} - 1 \tag{15}$$

Replacing the exponential term:

$$\prod_{i<j} e^{-\beta U(r_{ij})} = \prod_{i<j}(1 + f(r_{ij})) = 1 + \sum_{i<j} f(r_{ij}) + \sum_{\text{pairs}} f(r_{ij}) f(r_{kl}) + \dots \tag{16}$$

For a dilute gas, we keep only the first-order term (interactions between pairs of particles). Since there are $\frac{N(N-1)}{2} \approx \frac{N^2}{2}$ such pairs, the spatial integral simplifies to:

$$\begin{aligned} \int d^{3N}r \left(1 + \sum_{i<j} f(r_{ij})\right) &= \int d^{3N}r + \frac{N^2}{2} \int d^{3N}r f(r_{12}) \\ &= V^N + \frac{N^2}{2} V^{N-1} \int d^3 r f(r) \end{aligned} \tag{17}$$

4 The Equation of State

Substituting this back into the total partition function:

$$\begin{aligned} Z_{\text{tot}}(N,V,T) &= Z_{\text{ideal}} \frac{1}{V^N} \left(V^N + \frac{N^2}{2} V^{N-1} \int d^3 r f(r) + \dots\right) \\ &= Z_{\text{ideal}} \left(1 + \frac{N^2}{2V} \int d^3 r f(r) + \dots\right) \\ &\approx Z_{\text{ideal}} \left(1 + \frac{N}{2V} \int d^3 r f(r) + \dots\right)^N \end{aligned} \tag{18}$$

This last steps is a bit of a jump in complexity, but it turns out to be exact once all higher-order terms are taken into account. Z_{tot} needs to be of that form to make sure that the free energy is extensive, that is, it scales with N. Now, we compute the Helmholtz free energy $F = -k_B T \ln Z_{\text{tot}}$:

$$\begin{aligned} F &= -k_B T \ln Z_{\text{ideal}} - N k_B T \ln \left(1 + \frac{N}{2V} \int d^3 r f(r) + \dots\right) \\ &= F_{\text{ideal}} + F_{\text{new}} \end{aligned} \tag{19}$$

Using the small-argument approximation $\ln(1+x) \approx x$:

$$F \approx F_{\text{ideal}} - \frac{N^2 k_B T}{2V} \int d^3 r f(r) \tag{20}$$

The pressure is given by $P = -\frac{\partial F}{\partial V}$:

$$\begin{aligned} P &= -\frac{\partial F_{\text{ideal}}}{\partial V} - \frac{\partial F_{\text{new}}}{\partial V} \\ &= \frac{N k_B T}{V} + N k_B T \left(-\frac{N}{2V^2}\right) \int d^3 r f(r) + \dots \\ &= \frac{N k_B T}{V} \left[1 - \frac{N}{2V} \int d^3 r f(r) + \dots\right] \end{aligned} \tag{21}$$

Comparing this to the virial expansion, we identify the **second virial coefficient**:

$$\boxed{B_2(T) = -\frac{1}{2} \int d^3 r f(r)} \tag{22}$$

5 Evaluating the Hard-Core Potential

For the hard-core plus attractive potential described earlier, we evaluate the spatial integral of the Mayer f-function:

$$\int d^3r f(r) = \int_0^{r_0} d^3r(e^{-\beta(\infty)} - 1) + \int_{r_0}^{\infty} d^3r \left(e^{\beta U_0 (r_0/r)^6} - 1\right) \tag{23}$$

Since $e^{-\infty} = 0$, the first term (the hard-core repulsion) evaluates to:

$$\int_0^{r_0} d^3r(-1) = -\frac{4\pi}{3} r_0^3 \equiv -2b \tag{24}$$

(where b represents the excluded volume per particle).

For the second term (the attractive tail), assuming temperatures are high enough that $\beta U_0 \ll 1$, we can Taylor expand the exponential $e^x - 1 \approx x$:

$$\begin{aligned}
\int_{r_0}^{\infty} 4\pi r^2 dr \left(\beta U_0 \frac{r_0^6}{r^6}\right) &= 4\pi\beta U_0 r_0^6 \int_{r_0}^{\infty} r^{-4} dr \\
&= 4\pi\beta U_0 r_0^6 \left[\frac{r^{-3}}{-3}\right]_{r_0}^{\infty} \\
&= \frac{4\pi}{3} \beta U_0 r_0^3 \equiv 2a\beta
\end{aligned} \tag{25}$$

Putting it all together, the integral is $\int d^3r f(r) = -2b + 2a\beta$. The second virial coefficient is therefore:

$$B_2(T) = b - \frac{a}{k_B T}. \tag{26}$$

Substituting this back into our equation of state:

$$P \approx \frac{N k_B T}{V} \left[1 + \frac{N}{V}\left(b - \frac{a}{k_B T}\right)\right]. \tag{27}$$

This is the first-order statistical derivation of the famous **van der Waals equation of state**. This can also be written as

$$\boxed{\left(P + \frac{N^2}{V^2} a\right)(V - Nb) = N k_B T} \tag{28}$$