

5.2: Quantum Ideal Gases - Low Density Expansions

Expansion in powers of the fugacity

From Equation [numeqn], we have that the number density $n = N/V$ is

$$\begin{aligned} n(T, z) &= \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{z^{-1} e^{\varepsilon/k_B T} \mp 1} \\ &= \sum_{j=1}^{\infty} (\pm 1)^{j-1} C_j(T) z^j, \end{aligned}$$

where $z = \exp(\mu/k_B T)$ is the fugacity and

$$C_j(T) = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) e^{-j\varepsilon/k_B T}. \quad (5.2.1)$$

From $\Omega = -pV$ and our expression above for $\Omega(T, V, \mu)$, we have

$$\begin{aligned} p(T, z) &= \mp k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \ln \left(1 \mp z e^{-\varepsilon/k_B T} \right) \\ &= k_B T \sum_{j=1}^{\infty} (\pm 1)^{j-1} j^{-1} C_j(T) z^j. \end{aligned}$$

Virial expansion of the equation of state

Eqns. ??? and ??? express $n(T, z)$ and $p(T, z)$ as power series in the fugacity z , with T -dependent coefficients. In principal, we can eliminate z using Equation ???, writing $z = z(T, n)$ as a power series in the number density n , and substitute this into Equation ??? to obtain an equation of state $p = p(T, n)$ of the form

$$p(T, n) = n k_B T \left(1 + B_2(T) n + B_3(T) n^2 + \dots \right). \quad (5.2.2)$$

Note that the low density limit $n \rightarrow 0$ yields the ideal gas law independent of the density of states $g(\varepsilon)$. This follows from expanding $n(T, z)$ and $p(T, z)$ to lowest order in z , yielding $n = C_1 z + \mathcal{O}(z^2)$ and $p = k_B T C_1 z + \mathcal{O}(z^2)$. Dividing the second of these equations by the first yields $p = n k_B T + \mathcal{O}(n^2)$, which is the ideal gas law. Note that $z = n/C_1 + \mathcal{O}(n^2)$ can formally be written as a power series in n .

Unfortunately, there is no general analytic expression for the virial coefficients $B_j(T)$ in terms of the expansion coefficients $n_j(T)$. The only way is to grind things out order by order in our expansions. Let's roll up our sleeves and see how this is done. We start by formally writing $z(T, n)$ as a power series in the density n with T -dependent coefficients $A_j(T)$:

$$z = A_1 n + A_2 n^2 + A_3 n^3 + \dots \quad (5.2.3)$$

We then insert this into the series for $n(T, z)$:

$$\begin{aligned} n &= C_1 z \pm C_2 z^2 + C_3 z^3 + \dots \\ &= C_1 (A_1 n + A_2 n^2 + A_3 n^3 + \dots) \pm C_2 (A_1 n + A_2 n^2 + A_3 n^3 + \dots)^2 \\ &\quad + C_3 (A_1 n + A_2 n^2 + A_3 n^3 + \dots)^3 + \dots \end{aligned}$$

Let's expand the RHS to order n^3 . Collecting terms, we have

$$n = C_1 A_1 n + (C_1 A_2 \pm C_2 A_1^2) n^2 + (C_1 A_3 \pm 2C_2 A_1 A_2 + C_3 A_1^3) n^3 + \dots \quad (5.2.4)$$

In order for this equation to be true we require that the coefficient of n on the RHS be unity, and that the coefficients of n^j for all $j > 1$ must vanish. Thus,

$$\begin{aligned}C_1 A_1 &= 1 \\C_1 A_2 \pm C_2 A_1^2 &= 0 \\C_1 A_3 \pm 2C_2 A_1 A_2 + C_3 A_1^3 &= 0.\end{aligned}$$

The first of these yields A_1 :

$$A_1 = \frac{1}{C_1}. \quad (5.2.5)$$

We now insert this into the second equation to obtain A_2 :

$$A_2 = \mp \frac{C_2}{C_1^3}. \quad (5.2.6)$$

Next, insert the expressions for A_1 and A_2 into the third equation to obtain A_3 :

$$A_3 = \frac{2C_2^2}{C_1^5} - \frac{C_3}{C_1^4}. \quad (5.2.7)$$

This procedure rapidly gets tedious!

And we're only half way done. We still must express p in terms of n :

$$\begin{aligned}\frac{p}{k_B T} &= C_1 (A_1 n + A_2 n^2 + A_3 n^3 + \dots) \pm \frac{1}{2} C_2 (A_1 n + A_2 n^2 + A_3 n^3 + \dots)^2 \\&\quad + \frac{1}{3} C_3 (A_1 n + A_2 n^2 + A_3 n^3 + \dots)^3 + \dots \\&= C_1 A_1 n + (C_1 A_2 \pm \frac{1}{2} C_2 A_1^2) n^2 + (C_1 A_3 \pm C_2 A_1 A_2 + \frac{1}{3} C_3 A_1^3) n^3 + \dots \\&= n + B_2 n^2 + B_3 n^3 + \dots\end{aligned}$$

We can now write

$$\begin{aligned}B_2 &= C_1 A_2 \pm \frac{1}{2} C_2 A_1^2 = \mp \frac{C_2}{2C_1^2} \\B_3 &= C_1 A_3 \pm C_2 A_1 A_2 + \frac{1}{3} C_3 A_1^3 = \frac{C_2^2}{C_1^4} - \frac{2C_3}{3C_1^3}.\end{aligned}$$

It is easy to derive the general result that $\boxed{B^{\text{ssr}\{F\}}_j = (-1)^{j-1} B^{\text{ssr}\{B\}}_j}$, where the superscripts denote Fermi (F) or Bose (B) statistics.

We remark that the equation of state for classical (and quantum) *interacting* systems also can be expanded in terms of virial coefficients. Consider, for example, the van der Waals equation of state,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T. \quad (5.2.8)$$

This may be recast as

$$\begin{aligned}p &= \frac{nk_B T}{1 - bn} - an^2 \\&= nk_B T + (bk_B T - a)n^2 + k_B T b^2 n^3 + k_B T b^3 n^4 + \dots,\end{aligned}$$

where $n = N/V$. Thus, for the van der Waals system, we have $B_2 = (bk_B T - a)$ and $B_k = k_B T b^{k-1}$ for all $k \geq 3$.

Ballistic Dispersion

For the ballistic dispersion $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$ we computed the density of states in Equation ??? . One finds

$$C_j(T) = \frac{g_S \lambda_T^{-d}}{\Gamma(d/2)} \int_0^\infty dt t^{\frac{d}{2}-1} e^{-jt} = g_S \lambda_T^{-d} j^{-d/2}. \quad (5.2.9)$$

We then have

$$B_2(T) = \mp 2^{-\left(\frac{d}{2}+1\right)} \cdot g_S^{-1} \lambda_T^d$$

$$B_3(T) = \left(2^{-(d+1)} - 3^{-\left(\frac{d}{2}+1\right)}\right) \cdot 2 g_S^{-2} \lambda_T^{2d}.$$

Note that $B_2(T)$ is negative for bosons and positive for fermions. This is because bosons have a tendency to bunch and under certain circumstances may exhibit a phenomenon known as *Bose-Einstein condensation* (BEC). Fermions, on the other hand, obey the Pauli principle, which results in an extra positive correction to the pressure in the low density limit.

We may also write

$$n(T, z) = \pm g_S \lambda_T^{-d} Li_{\frac{d}{2}}(\pm z) \quad (5.2.10)$$

and

$$p(T, z) = \pm g_S k_B T \lambda_T^{-d} Li_{\frac{d}{2}+1}(\pm z), \quad (5.2.11)$$

where

$$Li_q(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^q} \quad (5.2.12)$$

is the *polylogarithm function*². Note that $Li_q(z)$ obeys a recursion relation in its index, viz.

$$z \frac{\partial}{\partial z} Li_q(z) = Li_{q-1}(z), \quad (5.2.13)$$

and that

$$Li_q(1) = \sum_{n=1}^{\infty} \frac{1}{n^q} = \zeta(q). \quad (5.2.14)$$

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