

## 7.5: Equation of State

The equation of state, as given by Equation 7.4.19, requires the computation of the grand canonical partition function. We will consider the case where the only conserved quantities are the Hamiltonian and the number of particles. The grand canonical partition function can then be written as

$$Z = \sum_{N=0}^{\infty} z^N Q_N = 1 + \sum_{N=1}^{\infty} z^N Q_N \quad z = e^{\beta\mu} \quad (7.5.1)$$

where  $Q_N$  is the canonical partition for a fixed number of particles, given in Equation 7.4.12. The variable  $z = e^{\beta\mu}$  is called the fugacity. The easiest way to proceed to the equation of state is to consider an expansion of  $\log Z$  in powers of  $z$ . This is known as the cumulant expansion and, explicitly, it takes the form

$$\log \left[ 1 + \sum_{N=1}^{\infty} z^N Q_N \right] = 1 + \sum_{n=1}^{\infty} z^n a_n \quad (7.5.2)$$

where the first few coefficients are easily worked out as

$$\begin{aligned} a_1 &= Q_1 \\ a_2 &= Q_2 - \frac{1}{2} Q_1^2 \\ a_3 &= Q_3 - Q_2 Q_1 + \frac{1}{3} Q_1^3 \end{aligned} \quad (7.5.3)$$

The Hamiltonian, for  $N$  particles, has the form

$$H_N = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} V(x_i, x_j) + \dots \quad (7.5.4)$$

where we have included a general two-particle interaction and the ellipsis stands for possible 3-particle and higher interactions. For  $N = 1$  we just have the first term. The  $p$ -integrations factorize and, if  $V(x_i, x_j) = 0$ , we get  $Q_N = \frac{Q_1^N}{N!}$ . All cumulants  $a_n$  vanish except for  $a_1$ . We can explicitly obtain

$$a_1 = Q_1 = \int \frac{d^3 x_i d^3 p_i}{(2\pi\hbar)^3} \exp \left( -\frac{\beta p_i^2}{2m} \right) = V \left( \frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} \quad (7.5.5)$$

For  $Q_2$ , we find

$$\begin{aligned} Q_2 &= \frac{1}{2!} \frac{Q_1^2}{V^2} \int d^3 x_1 d^3 x_2 e^{-\beta V(x_1, x_2)} \\ &= \frac{Q_1^2}{2V} \int d^3 x e^{-\beta V(x)} \end{aligned} \quad (7.5.6)$$

where, in the second line, we have taken the potential to depend only on the difference  $\vec{x}_1 - \vec{x}_2$  and carried out the integration over the center of mass coordinate. Thus

$$a_2 = \frac{Q_1^2}{2V} \int d^3 x \left( 1 - e^{-\beta V(x)} \right) \quad (7.5.7)$$

Using the cumulant expansion to this order, we find  $\log Z \approx zQ_1 + z^2 a_2$  and the average number of particles in the volume  $V$  is given by

$$\bar{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z \approx zQ_1 + z^2 a_2 \quad (7.5.8)$$

which can be solved for  $z$  as

$$zQ_1 \approx \bar{N} - 2a_2 \frac{\bar{N}^2}{Q_1^2} + \dots \quad (7.5.9)$$

If we ignore the  $a_2$ -term, this relation is the same as what we found in Equation 7.2.14, with the addition of the  $(2\pi\hbar)^3$  correction,

$$\beta\mu = \log \left[ \frac{\bar{N}}{V} \left( \frac{2\pi\hbar^2}{mkT} \right) \right] \quad (7.5.10)$$

Using Equation 7.5.9 (with the  $a_2$ -term) back in  $\log Z$  and the expression 7.5.7 for  $a_2$ , we get

$$\begin{aligned} \frac{pV}{\bar{N}kT} &\approx \left[ 1 + \frac{\bar{N}}{V} B_2 + \dots \right] \\ B_2 &= \frac{1}{2} \int d^3x \left( 1 - e^{-\beta V(x)} \right) \end{aligned} \quad (7.5.11)$$

These formulae show explicitly the first correction to the ideal gas equation of state. The quantity  $B_2$  is a function of temperature; it is called the **second virial coefficient** and can be calculated, once a potential is known, by carrying out the integration. Even for complicated potentials it can be done, at least, numerically. As a simple example, consider a hard sphere approximation to the interatomic potential,

$$V(r) = \begin{cases} \infty & r < r_0 \\ 0 & r > r_0 \end{cases} \quad (7.5.12)$$

In this case the integral is easily done to obtain  $B_2 = \left( \frac{2\pi r_0^3}{3} \right)$ . This is independent of the temperature. One can consider more realistic potentials for better approximations to the equation of state.

The van der Waals equation, which we considered earlier, is, at best, a model for the equation of state incorporating some features of the interatomic forces. Here we have a more systematic way to calculate with realistic interatomic potentials. Nevertheless, there is a point of comparison which is interesting. If we expand the van der Waals equation in the form in Equation 7.5.11, it has  $B_2 = b - \left( \frac{a}{kT} \right)$ ; the term  $b$  is independent of the temperature. Comparing with the hard sphere repulsion at short distances, we see how something like the excluded volume effect can arise.

We have considered the first corrections due to the interatomic forces. More generally, the equation of state takes the form

$$\frac{pV}{\bar{N}kT} = \left[ 1 + \sum_{n=2}^{\infty} \left( \frac{\bar{N}}{V} \right)^{n-1} B_n \right] \quad (7.5.13)$$

This is known as the **virial expansion**, with  $B_n$  referred to as the  $n$ -th virial coefficient. These are in general functions of the temperature; they can be calculated by continuing the cumulant expansion to higher order and doing the integrations needed for  $Q_N$ . In practice such a calculation becomes more and more difficult as  $N$  increases. This virial expansion in Equation 7.5.13 is in powers of the density  $\frac{\bar{N}}{V}$  and integrations involving powers of  $e^{-\beta V_{int}}$ , where  $V_{int}$  is the potential energy of the interaction. Thus for low densities and interaction strengths small compared to  $kT$ , truncation of the series at some finite order is a good approximation. So only a few of the virial coefficients are usually calculated.

It is useful to calculate corrections to some of the other quantities as well. From the identification of  $\bar{N}$  in Equation 7.5.8 and from Equation 7.4.16, we can find the internal energy as

$$U = \frac{3}{2} \bar{N} kT + \frac{\bar{N}^2}{2V} \int d^3x V(x) e^{-\beta V(x)} + \dots \quad (7.5.14)$$

In a similar way, the entropy is found to be

$$\bar{S} = \bar{N} k \left[ \frac{5}{2} + \log \frac{V}{\bar{N}} + \frac{3}{2} \log \left( \frac{mkT}{2\pi\hbar^2} \right) + \frac{\bar{N}}{2V} \int d^3x \left( \beta V(x) e^{-\beta V(x)} - 1 + e^{-\beta V(x)} \right) \right] \quad (7.5.15)$$

Since the number of pairs of particles is  $\approx \frac{\bar{N}^2}{2}$ , the correction to the internal energy is easily understood as an average of the potential energy. Also the first set of terms in the entropy reproduces the Sackur-Tetrode formula (7.2.25) for an ideal gas.

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