Ex5023: Pressure of hard spheres

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The problem:

Consider a one-dimensional classical gas of N particles in a length L at temperature T. The particles have mass m and interact via a 2-body "hard sphere" interaction (x_i is the position of the i-th particle):

$$\begin{aligned} V(x_i - x_j) &= \infty \qquad\qquad |x_i - x_j| < a \\ &= 0 \qquad\qquad |x_i - x_j| > a \end{aligned}$$

(a) Evaluate the exact free energy $F(T, L, N)$.

(b) Find the equation of state and identify the first virial coefficient; compare with its direct definition.

(c) Show that the energy is $E = Nk_BT/2$. Why is there no effect of the interactions on E ?

The solution:

(a) The Hamiltonian of the system is $\mathcal{H} = \sum\limits_{i=1}^{N} \frac{p_i^2}{2m} + \sum\limits_{<i,j>} V_{i,j}$, where $V_{i,j}$ is the "hard sphere" interaction between particle i and j, as introduced in the question.

Writing the partition function, we have:

$$Z_N = \frac{1}{N!}\int dx_1...dx_N dp_1...dp_N e^{-\beta\mathcal{H}} = \frac{1}{N!}\left(\frac{1}{\lambda_T}\right)^N \int\limits_0^L dx_1...dx_N e^{-\beta \sum\limits_{<i,j>} V_{i,j}} \tag{1}$$

Notice that the integrand is either 1 in case of 'non-overlapping' particles or 0 otherwise (taking a as their diameter). This means that every integral describes the volume which is unoccupied by the particles, i.e. $L - aN$. It immediately follows that:

$$Z_N = \frac{1}{N!}\left(\frac{L - aN}{\lambda_T}\right)^N \tag{2}$$

Thus, the free energy is:

$$F = -T\ln Z_N = T\left(\ln N! - N\ln\frac{L - aN}{\sqrt{2\pi\beta/m}}\right) \tag{3}$$

here we replaced λ_T by its definition: $\sqrt{2\pi\beta/m}$.

(b) Let us derive the pressure:

$$P = \frac{1}{\beta}\frac{\partial \ln Z_N}{\partial L} = \frac{NT}{L - aN} = \frac{NT}{L}\left(\frac{1}{1 - \frac{aN}{L}}\right) = \frac{NT}{L}\sum_{i=0}^{\infty} a^i\left(\frac{N}{L}\right)^i \tag{4}$$

The relation between the temperature, pressure and volume is the equation of state.
By inspetion, the first (non-trivial) virial coefficient is a. Calculating the virial coefficient directly gives

$$a_2 = -\frac{\lambda_T^2}{2!L}\left(Z_2 - Z_1^2\right) = -\frac{1}{2L}\left(\int dx_1 dx_2 e^{-\beta V_{1,2}} - L^2\right) \tag{5}$$

Where the last integral can be computed as the area in the position space corresponding to $|x_1 - x_2| > a$ within $[0, L]^2$, which is $(L-a)^2$. Finally, the virial coefficient is:

$$a_2 = \frac{1}{2L}\left((L-a)^2 - L^2\right) \approx a \tag{6}$$

The last statement holds for $a \ll L$, which is true in the thermodynamic limit.

(c) Calculating the enrgy we have:

$$E = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{N}{\sqrt{\beta}}\frac{1}{2\sqrt{\beta}} = \frac{NT}{2} = \frac{N(k_B)T}{2} \tag{7}$$

This is the exact energy for a gas with no interactions. This energy comes from the equipartition of energy, i.e. the square of the momentum. This system describes spheres which only collide elastically (hard core potential), so this energy is conserved and remains $\frac{N(k_B)T}{2}$. There is no energy scale associate with the repulsive interaction, so one should not expect another energy term.