Virial expansion hard sphere

Problem Statement

Consider a classical gas of particles with a "hard-sphere potential" - just think of balls on a pool table, and note that one ball does not penetrate any other ball. The simple inter-particle potential for this situation is given by

$$u(r) = \begin{cases} \infty & \text{if } r < \sigma \\ 0 & \text{if } r > \sigma \end{cases}$$

The virial expansion of such a fluid is such that the virial expansion coefficients must be independent of T - simply put, $k_B T$ is insignificant in comparison to the height of the inter-particle potential $u(r)$. Therefore,

$$\frac{P}{k_B T} = \rho + B_2\rho^2 + B_3\rho^3 + \dots$$

(a) Show that $B_2 = \frac{2}{3}\pi\sigma^3$. Argue that this potential gives rise to an excluded volume given by $V_{ex} = N\frac{2}{3}\pi\sigma^3$.

(b) One may then express the higher-order coefficients in terms of B_2. These have been calculated exactly up to B_{10}. Here we study an approximation which gives results very close to the exact coefficients (at least up to $n = 10$). This approximation leads to the following expansion:

$$\frac{PV}{Nk_B T} = 1 + 4x + 10x^2 + 18x^3 + 28x^4 + 40x^5 \dots$$

where

$$x \equiv \frac{NB_2}{4V}$$

Note that this series corresponds to the following choice for the "reduced" virial expansion coefficients:

$$b_n = n(n+3) \quad \text{with} \quad \frac{PV}{Nk_B T} = 1 + \sum_{n=1}^{\infty} b_n x^n$$

Exactly re-sum the resulting series (to infinite order), thereby obtaining an approximate equation of state for the hard-sphere system. Plot $PV/(Nk_B T)$ as a function of σ^3, and comment on your result. (For example, why is the pressure increased or decreased relative to an ideal gas?)

Solution.(a)

We can start with the fact that our Hamiltonian will be given by,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} U\left(r_{ij}\right) \tag{44}$$

The (classical) partition function is then given by,

$$\begin{aligned}
Z(N,V,T) &= \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^{N} d^3p_i d^3r_i e^{-\beta H} \\
&= \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \left[\int \prod_i d^3p_i e^{-\beta \sum_j p_j^2/2m}\right] \times \left[\int \prod_i d^3r_i e^{-\beta \sum_{j<k} U\left(r_{jk}\right)}\right] \\
&= \frac{1}{N!\lambda^{3N}} \int \prod_i d^3r_i e^{-\beta \sum_{j<k} U\left(r_{jk}\right)}
\end{aligned}$$

where λ is the thermal wavelength as before.

The integral there looks fierce and don't factor easily. One way would be to lay back to our friendly Taylor expansion, but it doesn't really turn out useful in general. Instead we will work with **Mayer f function**, given by

$$f(r) = e^{-\beta U(r)} - 1 \tag{45}$$

For our potential which is given by,

$$U(r) = \begin{cases} \infty & \text{if } r < \sigma \\ 0 & \text{if } r > \sigma \end{cases} \tag{46}$$

This gives us our Mayer f function to be,

$$f(r) = \begin{cases} -1 & \text{if } r < \sigma \\ 0 & \text{if } r > \sigma \end{cases} \tag{47}$$

We will write down a suitable expansion in terms of f by defining $f_{ij} = f(r_{ij})$

Then we can write the partition function as

$$\begin{aligned}
Z(N,V,T) &= \frac{1}{N!\lambda^{3N}} \int \prod_i d^3r_i \prod_{j>k} (1+f_{jk}) \\
&= \frac{1}{N!\lambda^{3N}} \int \prod_i d^3r_i \left(1 + \sum_{j>k} f_{jk} + \sum_{j>k,l>m} f_{jk}f_{lm} + \dots\right)
\end{aligned}$$

The first term simply gives a factor of the volume V for each integral, so we get V^N. The second term has a sum, each element of which is the same. They all look like

$$\int \prod_{i=1}^{N} d^3 r_i f_{12} = V^{N-2} \int d^3 r_1 d^3 r_2 f\left(r_{12}\right) = V^{N-1} \int d^3 r f(r)$$

where, in the last equality, we've simply changed integration variables from $\vec{r}_1$ and $\vec{r}_2$ to the center of mass $\vec{R} = \frac{1}{2}\left(\vec{r}_1 + \vec{r}_2\right)$ and the separation $\vec{r} = \vec{r}_1 - \vec{r}_2$.

Ignoring terms quadratic in f and higher, we approximately have,

$$\begin{aligned} Z(N, V, T) &= \frac{V^N}{N! \lambda^{3N}} \left(1 + \frac{N^2}{2V} \int d^3 r f(r) + \ldots\right) \\ &= Z_{\text{ideal}} \left(1 + \frac{N}{2V} \int d^3 r f(r) + \ldots\right)^N \end{aligned} \tag{48}$$

where,

$$Z_{\text{ideal}} = V^N / N! \lambda^{3N} \tag{49}$$

From here, we have a free energy expression,

$$F = -k_B T \log Z = F_{\text{ideal}} - N k_B T \log\left(1 + \frac{N}{2V} \int d^3 r f(r)\right) \tag{50}$$

Expanding the logarithm for $\log(1+\epsilon)\, a \approx \epsilon$

$$p = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V} \left(1 - \frac{N}{2V} \int d^3 r f(r) + \ldots\right) \tag{51}$$

As we can see, the pressure is deviating from ideal gas by a correction,

$$\frac{pV}{N k_B T} = 1 - \frac{N}{2V} \int d^3 r f(r) \tag{52}$$

Now, we will just use the Mayer f function that we have defined earlier to get,

$$\int d^3 r f(r) = -4\pi \int_0^{\sigma} + 0 \tag{53}$$

$$= -\frac{4\pi\sigma^3}{3} \tag{54}$$

$$\tag{55}$$

Plugging this into the ideal gas law with corrections eq.(50) , we see

$$b = \frac{2\pi\sigma^3}{3} \tag{56}$$

(I might have gone a little overboard for this problem..)

Nevertheless, I still have to show that this gives rise to the required V_{ex} volume.

$$\frac{P}{k_B T} = \rho + \frac{2\pi\sigma^3}{3}\rho^2 \tag{57}$$

$$= \frac{N}{V} + \frac{2\pi\sigma^3 N}{3} N \tag{58}$$

$$= \frac{N}{V}\left(1 + \frac{V_{\text{ex}}}{V}\right) \tag{59}$$

giving us that,

$$V_{\text{ex}} = \frac{2}{3}\pi N\sigma^3 \tag{60}$$

Solution.(b)

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ClearAll["Global`*"]
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In[23]:=
```
FindGeneratingFunction[{1, 4, 10, 18, 28, 40}, n]
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Out[23]=

$$1+\frac{2\ (-2+n)\ n}{(-1+n)^{3}}$$

This gives us,

In[20]:= $\texttt{y[x\_] = 1} + \sum_{n=1}^{\infty} (n)\ (n+3)\ x^{n}$

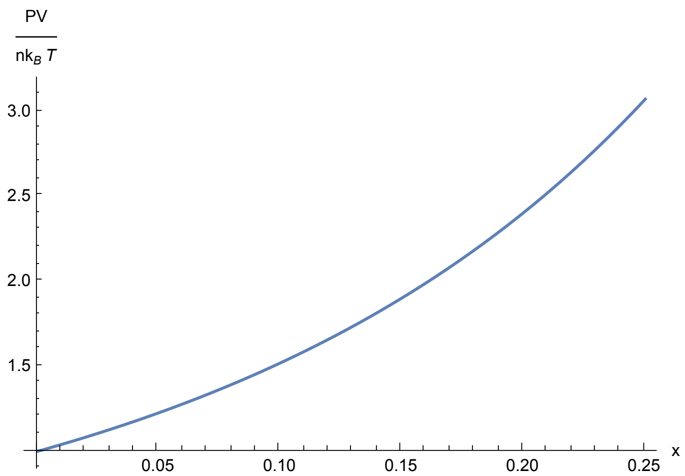
Out[20]=

$$1+\frac{2\ (-2+x)\ x}{(-1+x)^{3}}$$

In[17]:= $\texttt{Plot}\left[1+\frac{2\ (-2+x)\ x}{(-1+x)^{3}},\ \{x,\ -8,\ 8\}\right]$

In[25]:= $\texttt{Plot}\left[1+\frac{2\ (-2+x)\ x}{(-1+x)^{3}},\ \left\{x,\ 0,\ \frac{1}{4}\right\},\ \texttt{AxesLabel} \to \left\{\texttt{"x"},\ \texttt{"}\frac{PV}{nk_{B}\ T}\texttt{"}\right\}\right]$

Out[25]=



In comparison to ideal gas, the pressure is high, which makes sense as the collisions between the hard spheres can increase the pressure. (Also we plot the graph only from $x = 0$ to $x = \frac{1}{4}$, because after that we go into the domain of $V_{ex} > V$ which doesn't make sense)