Bose-Einstein Condensate (1)

Problem

Does BEC occur in 1d or 2d (for free particles using periodic boundary conditions)? Prove your answers with complete calculations.

Solution.

Our goal for this problem is to check if BEC occurs for 1D and 2D with periodic boundary conditions. I want to start with the 2D case.

One crucial point where we get BEC in the 3D case is from the density of states (DOS). Particularly, we realize that we approximated the sum for DOS to an integral without considering the zero energy modes of our system. The zero energy modes become more and more relevant when the temperature keeps dropping or rather when the fugacity $z \to 1$ (this is the low-temperature limit). So to take care of these missed states, we put a correction factor in the number density, and after working out some algebra for this new number density, we establish that BECs must exist in the 3D case.

So to start from the bottom in the case of 1D or 2D, we need to go back to the definition of DOS in those dimensions.

Starting with 2D:

The energy eigenstates for particles in a box of length L and periodic boundary conditions is given by,

$$\psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}}, \tag{1}$$

where $V = L^2$ and the wavevector $\vec{k} = (k_1, k_2)$ are quantized as

$$k_i = \frac{2\pi n_i}{L}, \quad n_i \in \mathbb{Z}, \tag{2}$$

and the energy of the particle is given by,

$$E_{\vec{n}} = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2\hbar^2}{2mL^2}\left(n_1^2 + n_2^2\right) \tag{3}$$

where $k = \left|\vec{k}\right|^2$

The quantum mechanical single particle partition function is given by the sum over all energy eigenstates,

$$Z_1 = \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} \tag{4}$$

Comment

Now the main question here is how to evaluate the sum. The usual way is to approximate this sum with an integral. The way we come to this approximation is first by recalling that

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} \tag{5}$$

is the thermal wavelength of a particle. Now looking at Z_1, we can see that we have exponentiated the energy, which in terms of this wavelength can be written as,

$$\beta E_{\vec{n}} = \beta\frac{4\pi^2\hbar^2}{2mL^2}n^2 = \frac{1}{k_BT}\frac{\lambda^2 k_BT}{L^2}n^2 = \frac{\lambda^2 n^2}{L^2} \tag{6}$$

For any macroscopic box (1 meter length) containing say a mole of particles at room temperature (293 K), $L \gg \lambda$ is true. This means that the exponent is an extremely small number. In other words, there are many states $E_{\vec{n}} < k_BT$, where all of them contribute to the sum.

This is the point where we say that we can approximate the sum to an integral (due to the the comment above),

$$\sum_n \approx \int d^3n = \frac{V}{(2\pi)^3}\int d^3k \tag{7}$$

This is true for 3D, for 2D we will have an integral over d^2k instead giving us,

$$\sum_n \approx \int d^2n = \frac{V}{(2\pi)^2}\int d^2\vec{k} \tag{8}$$

$$= \frac{V}{(2\pi)^2}\iint dk\, dk_\theta \tag{9}$$

$$= \frac{V}{(2\pi)^2}2\pi\int kdk \tag{10}$$

$$= \frac{V}{2\pi}\int kdk \tag{11}$$

$$\tag{12}$$

where we changed to polar coordinates.

At this point we want to change the integration variables from $k \to E$,

$$E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad dE = \frac{\hbar^2 k}{m} dk \quad \Rightarrow \quad kdk = \frac{m}{\hbar^2} dE \tag{13}$$

Now we are in a position to change the variables for the sum over n from $k \to E$,

$$\sum_n \approx \int d^2 n = \frac{V}{2\pi} \int kdk \tag{14}$$

$$= \frac{V}{2\pi} \int \frac{m}{\hbar^2} dE \tag{15}$$

$$= \int g(E) dE \tag{16}$$

Recall that by the definition of density of states, $g(E)dE$ corresponds to "number of states between $[E, E + dE]$." The integration over this quantity is exactly equivalent to the sum we have been talking about, explaining the last equality in the equation above.

This gives us the DOS in 2D to be,

$$g(E) = \frac{Vm}{2\pi\hbar^2} \tag{17}$$

Comment

I have not included the spin in the computation. We would have a factor of $(2S + 1)$ in front of the expression for $g(E)$ for a particle of spin S. The expression that we have for DOS is valid for spin 0 bosons.

An extremely analogous computation gives us the DOS in 1D,

$$\sum_k \to \int dn = \frac{l}{2\pi} \sqrt{\frac{2m}{\hbar^2}} \int \frac{1}{\sqrt{E}} dE \tag{18}$$

Unlike in the case of 3D, where the DOS is proportional to $\sqrt{E}$, for 1D and 2D we have DOS proportional to $(E)^{-\frac{1}{2}}$, constant respectively. These give rise to a divergent series (unlike $g_{\frac{3}{2}}(z)$ in the case of 3D. Giving us fact that, as temperature goes to zero, the number of states not in the ground state is non-zero and finitely large. This means, **we cannot have BEC in 1D and 2D**.

Bose Einstein Condensate (2)

Problem Statement

Which of the following is necessary to undergo Bose condensation at low temperatures?

(a) $g(E)/\left(e^{\beta(E-E_{\text{min}})}+1\right)$ is finite as $E \to E_{\text{min}}^-$.

(b) $g(E)/\left(e^{\beta(E-E_{\text{min}})}-1\right)$ is finite as $E \to E_{\text{min}}^-$.

(c) $E_{\text{min}} \geq 0$.

(d) $\int_{E_{\text{min}}}^{E} g(E')/(E'-E_{\text{min}})\,dE'$ is convergent at the lower limit E_{min}.

(e) Bose condensation cannot occur in a system whose states are confined to an energy band.

Solution

Looking at all the expressions we have to choose from, E, N are two quantities based on which I can talk about BEC conditions. I will start with N and see if I can make any conclusions, else move on to E. (I also have some motivation on starting with N because it is the form given the options plus, it is the primary parameter that decides whether we have BEC or not. The exact condition is what we wish to derive here.

Starting of with,

$$N = \int_{E_0}^{E_1} \frac{g(E)\,dE}{e^{\beta(E-\mu)}-1} \tag{19}$$

We get a singularity when $\mu \to E$. Another issue is when $\mu > E$ gives us negative N. This means that $\mu < E_0$ (For $E_1 > E_0$) throughout the integral. (We have a similar intuition from what we derived in (a) of this problem.

Recall that the main idea with BEC is that, as $z \to 1$, we start getting more and more particles settling in the ground state which were not accounted for when we use the approximation: $\sum_k \approx \int g(E)\,dE$. This means that, for us to have BEC, this integral must converge!

$$N = \int_{E_0}^{E_1} \frac{g(E)\,dE}{e^{\beta(E-E_0)}-1} < \infty \tag{20}$$

$$\tag{21}$$

I would already go for (d) to be the solution, but I see that the denominator is not agreeing with what I am saying (at least yet).

For $E_1 > E_0$, the place where I the BEC states are sitting in the integral are near E_0. Let $E_{00} = E_0 + \epsilon$ where $\epsilon > 0$ and is a small number.

$$N = \int_{E_0}^{E_{00}} \frac{g(E)\, dE}{e^{\beta(E-E_0)} - 1} + \int_{E_{00}}^{E_1} \frac{g(E)\, dE}{e^{\beta(E-E_0)} - 1} < \infty \tag{22}$$

$$\tag{23}$$

where we can see that the first term will be contributing much more than the second term due to the proximity of E_0, E_{00}

If we Taylor expand the exponential in the first term, the denominator will be $e^{\beta(E-E_0)} \approx 1 + \beta(E - E_0) + \mathcal{O}((E - E_0)^2) - 1$. Ignoring higher terms, we can see that the **case (d)**

$$\int_{E_0}^{E} \frac{g(E)\, dE}{E - E_0} < \infty \tag{24}$$

is our answer. I safely inserted $E_{00} \to E$ as for any $E > E_{00}$, it only helps the convergence of the integral.

Bose Einstein Condensate in 3D

Problem statement

Start with the following expression,

$$pV = k_B T \ln\left(\prod_k \left(\frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}\right)\right) = -k_B T \sum_k \ln\left(1 - z e^{-\beta\epsilon_k}\right)$$

and derive,

$$p = \frac{k_B T}{\lambda^3} \sum_{l=0}^{\infty} \frac{z^l}{l^{5/2}}$$

Solution

Given equation is,

$$pV = k_B T \ln\left(\prod_k \left(\frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}\right)\right) = -k_B T \sum_k \ln\left(1 - z e^{-\beta\epsilon_k}\right) \tag{25}$$

where I am using $z = e^{\beta\mu}$ as the fugacity.

Comment on BEC - Might need later

We recall that when we derive the Bose-Einstein distribution, we make the following approximation,

$$\sum_{\vec{k}} \approx \int g(E)\, dE \tag{26}$$

where

$$g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{27}$$

Because of the $\sqrt{E}$ in the integrand, $E = 0$ states are not taken into consideration when we do the sum over k. Those states become crucial when we drop the temperatures lower and lower (which is the basis of the BEC as we can recall learning in class). Using the Bose-Einstein distribution, we found that the correction needed (for the missing $E = 0$ states can be written as,

$$n_0 = \frac{1}{z^{-1} - 1} \tag{28}$$

For most of the values in $z \in (0, 1)$ the number of particles in n_0 is very low and the approximation for the sum to integral holds really well (as we are usually dealing with a set of particles as large as $\mathcal{O}(10^{23})$. But as $z \to 1$ the number of particles starts to get macroscopic.
For our current computations we are trying to mimic the derivation for Eq. 4.92 in the script. We carefully identify that, while deriving 4.92, $z \ll 1$ is an assumption made, and proceed for this part with the same assumption i.e. we assume eq.(26) is valid.

Handwritten solution continued on next page!

$$pV = -k_B T \sum_k \ln(1 - ze^{-\beta E_k}) = -k_B T \int g(E) \ln(1 - ze^{-\beta E_k})\, dE$$

Where, $g(E) = \varkappa E^{1/2}$, $\varkappa = \dfrac{V}{4\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$

$$= -\varkappa k_B T \underbrace{\int E^{1/2} \ln(1 - ze^{-\beta E})\, dE}_{I}$$

$$\boxed{\begin{aligned} &u = \ln(1 - ze^{-\beta E}), \quad \frac{du}{dE} = \frac{1}{1 - ze^{-\beta E}}(-ze^{-\beta E})(-\beta) \\ &\qquad\qquad\qquad\qquad du = \frac{\beta z e^{-\beta E}}{1 - ze^{-\beta E}}\, dE \\ &dv = E^{1/2} dE, \quad v = \int dv = \int E^{1/2} dE = \frac{2}{3} E^{3/2} \end{aligned}}$$

$$= -\varkappa k_B T \left[\underbrace{\frac{2}{3} \ln(1 - ze^{-\beta E}) E^{3/2} \Big|_0^\infty}_{} - \int \frac{2}{3} E^{3/2} \frac{\beta z e^{-\beta E}}{(1 - ze^{-\beta E})} dE \right]$$

This term goes to zero (Mathematica attached)

$$= \frac{2}{3} \varkappa \frac{\cancel{k_B T}}{\cancel{k_B T}} \int E^{3/2} \frac{1}{(z^{-1} e^{\beta E} - 1)} dE$$

$$= \frac{2}{3} \int \varkappa E^{1/2} \frac{E}{(z^{-1} e^{\beta E} - 1)} dE$$

$$= \frac{2}{3} \int \frac{g(E) E}{(z^{-1} e^{\beta E} - 1)} dE = \frac{2}{3} E$$

$$pV = \frac{2}{3}\int dE \; \frac{E\,g(E)}{z^{-1}e^{\beta E}-1}$$

$g(E) = \chi E^{1/2}$

$\chi = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$

Let $\beta E = x$; $\frac{dx}{dE} = \beta \Rightarrow dE = \frac{dx}{\beta}$

Integrat^n Bounds remain same.

$E = \frac{x}{\beta}$

$$= \frac{2}{3}\chi \int \frac{dx}{\beta} \frac{E^{3/2}}{z^{-1}e^{x}-1}$$

$$= \frac{2}{3}\chi \int \frac{dx}{\beta} \frac{1}{\beta^{3/2}} \frac{x^{3/2}}{z^{-1}e^{x}-1}$$

$$= \frac{2}{3}\frac{\chi}{\beta^{5/2}} \boxed{\int dx \frac{x^{3/2}}{z^{-1}e^{x}-1}} \rightarrow g_{5/2}(z)\,.\,\Gamma\left(\tfrac{5}{2}\right)$$

$$\frac{\chi}{\beta^{5/2}} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(k_BT)^{3/2}(k_BT) = \frac{V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2} k_BT$$

Recall that $\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$

$$= \frac{V}{4\pi^2}\left(\frac{2(2\pi)mk_BT}{(2\pi)\hbar^2}\right)^{3/2} k_BT$$

$$= \frac{V}{4\pi^2}(4\pi)^{3/2}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} k_BT$$

$$= V\frac{2}{\sqrt{\pi}}\frac{k_BT}{\lambda^3}$$

$$\therefore\; pV = \frac{2}{3}V\frac{2}{\sqrt{\pi}}\frac{k_BT}{\lambda^3}g_{5/2}(z)\,\Gamma\left(\tfrac{5}{2}\right) = \frac{4}{3\sqrt{\pi}}V\frac{k_BT}{\lambda^3}g_{5/2}(z)\,\Gamma(5/2)$$

We know $\Gamma\left(\frac{5}{2}\right) = \frac{3\sqrt{\pi}}{4}$ which cancels out the prefactor of $\frac{4}{3\sqrt{\pi}}$

$$\Rightarrow p\cancel{V} = \cancel{V}\frac{k_BT}{\lambda^3}g_{5/2}(z) \Rightarrow \quad p = \frac{k_BT}{\lambda^3}\sum_{l=0}^{\infty}\frac{z^l}{l^{5/2}}$$

$\square$

```
In[66]:= Limit[x^(3/2) Log[1 - z Exp[-x β]], x → 0, Assumptions → {β > 0, 0 < z < 1}]

Out[66]= 0

In[67]:= Limit[x^(3/2) Log[1 - z Exp[-x β]], x → ∞, Assumptions → {β > 0, 0 < z < 1}]

Out[67]= 0
```

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{z^{-1}e^x - 1} \tag{29}$$

Sometimes $g_n(z)$ is also represented by $\mathrm{Li}_n(z)$ these functions are called Polylogarithms. With some manipulation we can show that these Polylogarithms can be represented by a sum,

$$\begin{aligned} g_n(z) &= \frac{1}{\Gamma(n)} \int dx \frac{zx^{n-1}e^{-x}}{1 - ze^{-x}} \\ &= \frac{1}{\Gamma(n)} z \int dx x^{n-1} e^{-x} \sum_{m=0}^{\infty} z^m e^{-mx} \\ &= \frac{1}{\Gamma(n)} \sum_{m=1}^{\infty} z^m \int dx x^{n-1} e^{-mx} \\ &= \frac{1}{\Gamma(n)} \sum_{m=1}^{\infty} \frac{z^m}{m^n} \int du u^{n-1} e^{-u} \end{aligned} \tag{30}$$

The integral that appears in the last line above is nothing but the definition of the gamma function (n). This means that we can write,

$$g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n} \tag{31}$$

Solution 9.(b)

We know that BEC does not occur in 2D. Hence, we can safely use the $\sum_k \approx \int g(E)\, dE$ approximation.

$$E = \int \frac{g_{2\mathrm{D}}(E) E z e^{-\beta E}\, dE}{1 - ze^{-\beta E}} \tag{32}$$

$$= \frac{Vm}{2\pi\hbar^2} \sum_{i=1}^{\infty} z^{i+1} \int_0^\infty E e^{-\beta E(i+1)} \tag{33}$$

$$ \tag{34} $$

$$
\begin{aligned}
E &= \int \frac{g_{2\text{D}}(E)\, dE}{z^{-1}e^{\beta E} - 1} && (35)\\
&= \frac{Vm}{2\pi\hbar^2} \int \frac{dE}{z^{-1}e^{\beta E} - 1} && (36)\\
&= \frac{Vm}{2\pi\hbar^2\beta^2} && (37)\\
&= \frac{Vm}{2\pi\hbar^2\beta^2} \sum_{j=1}^{\infty} \frac{z^j}{j^2} && (38)
\end{aligned}
$$

Now its relation to PV is given by,

$$
\begin{aligned}
\frac{PV}{k_B T} &= -\sum_k \log\left(1 - ze^{-\beta E_k}\right) && (39)\\
&= -\frac{Vm}{2\pi\hbar^2} \int_0^{\infty} \log\left(1 - ze^{-\beta E}\right) dE && (40)\\
&= -\frac{Vm}{2\pi\hbar^2} \int dE \int d\beta \frac{Eze^{-\beta E}}{1 - ze^{-\beta E}} && (41)\\
&= -\frac{Vm}{2\pi\hbar^2} \int d\beta \frac{1}{\beta^2} \sum_{l=1}^{\infty} \frac{z^l}{l^2} && (42)
\end{aligned}
$$

Giving us,

$$ PV = E \tag{43} $$

Solution.(c) (1 page) + Solution.(d) (1 Page)

We have :
$$\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$
$$B_2(T) = -\left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right)\lambda^3$$

On the other side, we also know
$$\frac{P}{k_B T} = \frac{1}{\lambda^3}\left(z + \frac{z^2}{2^{3/2}} + \frac{z^3}{2^{5/2}} + \cdots\right)$$

Where , $z = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots$

From all this we have a relation between z & ρ.
$$\rho = \frac{1}{\lambda^3}\left[z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots\right]$$

- In order to get B_3, we first need a_3,
  - ↳ We get this by collecting all ρ^3 in → $\rho = \frac{1}{\lambda^3}\left(z + \frac{z^2}{2^{3/2}} + \frac{z^3}{2^{5/2}} + \cdots\right)$
  - ↳ $a_3 = \frac{\lambda^9}{4} - \frac{\lambda^9}{3\sqrt{3}}$

Last min Comment : Printing before class forgot to add Mathematica code here, Sorry!

Next → for B_3, we group ρ^3 term in :
$$\frac{PV}{k_B T} = \frac{1}{\lambda^3}\left(z + \frac{z^2}{2^{5/2}} + \cdots\right)$$
$$\frac{a_3}{\lambda^3} - \frac{\lambda^6}{8} + \frac{\lambda^6}{9\sqrt{3}} = B_3$$

Plug in a_3

$$\underline{B_3(T) = \left(\frac{9\sqrt{3} - 2}{72\sqrt{3}}\right)\lambda^6}$$

ROUGH PART

(i) $\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\, dT$

(ii) $C_V = T \frac{\partial S}{\partial T}\Big|_V$

(iii) $\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$

- We know from part (a) of this problem:

$$P = \frac{2}{3}\frac{E}{V} = \frac{k_B T}{\lambda^3} g_{5/2}(z)$$

$$= k_B T \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} g_{5/2}(z)$$

$$= k_B \left(\frac{m k_B}{2\pi\hbar^2}\right)^{3/2} T^{5/2}\, g_{5/2}(z)$$

$$\therefore E = \frac{3}{2}\left[k_B \left(\frac{m k_B}{2\pi\hbar^2}\right)^{3/2}\right] T^{5/2}\, g_{5/2}(z)\; V$$

We can plug this into

$$\frac{C_V}{V} = \frac{1}{V}\frac{dE}{dT} = \frac{3}{2}\left[k_B \left(\frac{m k_B}{2\pi\hbar^2}\right)^{3/2}\right] \frac{d}{dT}\left(T^{5/2} g_{5/2}(z)\right) \frac{\cancel{V}}{\cancel{V}}$$

$$= \frac{3}{2}\left[k_B \left(\frac{m k_B}{2\pi\hbar^2}\right)^{3/2}\right]\left(\frac{5}{2} T^{3/2} g_{5/2}(z) + T^{5/2} \frac{d g_{5/2}(z)}{dT}\right)$$

$$= \frac{15}{4} k_B \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} g_{5/2}(z) + \frac{3}{2} k_B T \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} \frac{d g_{5/2}(z)}{dz}\frac{dz}{dT}$$

$$= \frac{15}{4}\frac{k_B}{\lambda^3} g_{5/2}(z) + \frac{3}{2}\frac{k_B T}{\lambda^3}\frac{d g_{5/2}}{dz}\frac{dz}{dT}$$

$$\boxed{\text{As we have, } g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n} \Rightarrow \frac{d}{dz} g_n(z) = \frac{1}{z} g_{n-1}(z)}$$

$$= \underbrace{\frac{15}{4}\frac{k_B}{\lambda^3}}_{C_1} g_{5/2}(z) + \underbrace{\frac{3}{2}\frac{k_B T}{\lambda^3}\frac{1}{z}\frac{dz}{dT}}_{C_2} g_{3/2}(z)$$

- From eq^n.(ii) in the rough part (right top) of the page, we can see that for $\frac{S}{V}$ we will have the same relation with $C_1 \to \tilde{C}_1$ & $C_2 \to \tilde{C}_2$ (New prefactors)

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

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

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)

```
ClearAll["Global`*"]
```

In[23]:=
```
FindGeneratingFunction[{1, 4, 10, 18, 28, 40}, n]
```

Out[23]=

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

This gives us,

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

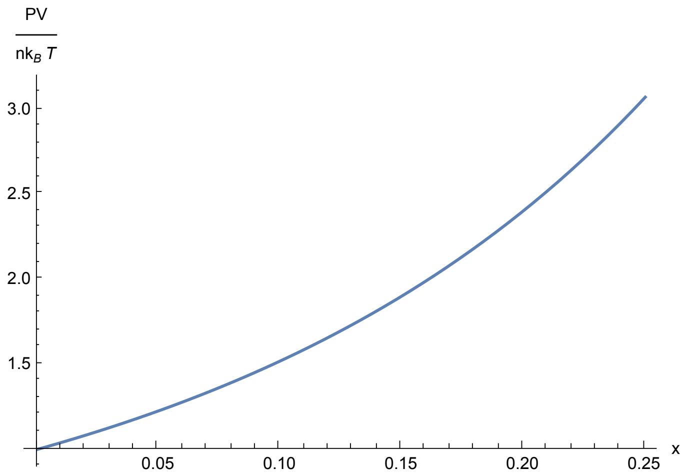
Out[20]=

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

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

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

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)