PHY 831: Statistical Mechanics
Homework 7

Due Wed Nov. 24 , 2021

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1. Find the 2nd virial coefficients b_2 for non-relativistic *non-interacting* quantum Fermi and Boson gases, working in the grand canonical ensemble. Now imagine a classical gas with some inter-particle potential $u(r)$ where r is the separation between two particles. Assuming $u(r)$ is a gaussian form, how would its range and strength have to be to chosen reproduce the results you got for the non-interacting Boson/Fermion gases?

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2. Consider a gas in d dimensions where the particles interact with the pairwise potential

$$\begin{aligned} u(r) &= +\infty \qquad \text{for } 0 < r < a \\ &= -u_0 \qquad \text{for } a < r < b \\ &= 0 \qquad \text{for } b < r < \infty \end{aligned} \tag{1}$$

10 (a) Calculate b_2 and comment on the high- and low-temperature behavior.

10 (b) Calculate the first correction to the isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{2}$$

10 (c) In the high-T limit, cast the equation of state into van der Waals form and identify the van der Waals parameters

20 (d) For $b = a$ (i.e., hard sphere potential) in $d = 1$, calculate the third virial coefficient b_3.

3. Given a system with the two-particle (or density-density) correlation function

$$g(R) = 1 + Ae^{-R/\ell}, \tag{3}$$

where A, and ℓ are constants, find the number fluctuations of the system,

$$\frac{\langle \Delta N^2 \rangle}{\langle N \rangle} = \frac{\langle N^2 - \langle N \rangle^2 \rangle}{\langle N \rangle}.$$

What is $\langle \Delta N^2 \rangle / N$ for a Boltzmann gas? What is $\langle \Delta N^2 \rangle / N$ for a non-interacting Fermi gas? [Calculate these directly from the grand canonical distribution function] Qualitatively, what does this tell us about spatial correlations in a Fermi gas?

(removed from HW due to cancelled class.

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* To get b_2 for non-interacting quantum gases (bosons/fermions), we use the definition of b_m as an expansion of $\log Z$ (GCE) in powers of fugacity z

$$\log Z = \frac{V}{v_Q} \sum_{m=1}^{\infty} b_m z^m$$

but $\log Z_\eta = -\eta V \int \frac{d^3k}{(2\pi)^3} \log\left(1 - \eta e^{-\beta(\epsilon_k - \mu)}\right)$

$\eta = +1$ Bosons
$\quad\ -1$ Fermions

$$= -\eta V \int \frac{d^3k}{(2\pi)^3} \log\left(1 - \eta z e^{-\beta\epsilon_k}\right)$$

Taylor expand $\log(1 - \eta z e^{-\beta\epsilon_k}) = -\eta z e^{-\beta\epsilon_k} - \frac{\eta^2 z^2}{2} e^{-2\beta\epsilon_k} + \cdots$

$$\therefore \frac{V}{v_Q} b_1 z + \frac{V}{v_Q} b_2 z^2 = -\eta V \int \frac{d^3k}{(2\pi)^3} \left(-\eta z e^{-\beta\epsilon_k} - \frac{z^2}{2} e^{-2\beta\epsilon_k} + \cdots\right)$$

Match powers of z:

z: $\Rightarrow \frac{V}{v_Q} b_1 z = zV \int \frac{d^3k}{(2\pi)^3} e^{-\frac{\beta\hbar^2k^2}{2m}} = z\frac{V}{v_Q} \Rightarrow b_1 = 1$

z^2: $\Rightarrow \frac{V}{v_Q} b_2 z^2 = \eta \frac{V z^2}{2} \int \frac{d^3k}{(2\pi)^3} e^{-\frac{\beta\hbar^2k^2}{m}} = \eta \frac{V z^2}{2^{5/2} v_Q} \Rightarrow \boxed{b_2 = \eta 2^{-5/2}}$

* To find a potential $u(r)$ for a classical gas that reproduces b_2 of the non-interacting boson/fermion gas, we use

$$b_2 = \frac{1}{2v_Q V}\left(Q_2 - Q_1^2\right)$$

<u>where</u> $Q_1 = V$ and $Q_2 = \int d\bar{r}_1 d\bar{r}_2 \, e^{-\beta u(r)}$

* Since the virial expansion is for high T, we can take $e^{-\beta u(r)} \simeq 1 - \beta u(r)$

$$\Rightarrow b_2 = \frac{1}{2v_Q V}\left(\cancel{V^2} - \beta \int d\bar{r}_1 d\bar{r}_2 \, u(r) - \cancel{V^2}\right)$$

let $\vec{R} = \frac{\bar{r}_1 + \bar{r}_2}{2}$; $\bar{r} = \bar{r}_1 - \bar{r}_2$

$$= \frac{-\beta}{2v_Q V} \cdot \underbrace{\int d\vec{R}}_{V} \int d\vec{r} \, u(r)$$

$\therefore$ Want to choose $u(r)$ so

$$b_2 = \eta \, 2^{-5/2} = \frac{-\beta}{2v_Q} \int d\vec{r} \, u(\vec{r}) \quad (*)$$

* per the problem statement, lets take $u(r) = u_0 e^{-r^2/a^2}$ & choose u_0 & a to satisfy eq. (*).

$$b_2 = \eta\, 2^{-5/2} = \frac{-\beta}{2v_Q} \int d\vec{r}\, u(\vec{r}) \quad (*)$$

$$= \frac{-\beta u_0}{2v_Q} \int d^3r\, e^{-r^2/a^2}$$

$$\boxed{\pm 2^{-5/2} = \frac{-\beta u_0}{2v_Q} \cdot \left(\pi a^2\right)^{3/2}}$$

(any combination of u_0 + a that satisfies this equation will match the b_2 of the non-interacting bose/fermi gas.

(we see the bose case is attractive, the fermion case is repulsive)

2.

a) $b_2 = \frac{1}{2v_\alpha V}\left(Q_2 - Q_1^2\right)$ (* here, $v_\alpha = l_\alpha^d$ & V is the d-dim. volume V_d.)

$$Q_1 = V_d = \int d^d r$$

$$Q_2 = \int d^d r_1 \, d^d r_2 \, e^{-\beta u(r_{12})} = V_d \int d^d r \, e^{-\beta u(r)}$$

$$\therefore b_2 = \frac{1}{2v_\alpha V_d}\left(V_d \int d^d r \, e^{-\beta u(r)} - V_d^2\right)$$

$$= \frac{1}{2v_\alpha}\left(\int d^d r \left(e^{-\beta u(r)} - 1\right)\right)$$

use $\int d^d r = \int d\Omega_d \int r^{d-1} dr = S_d \int r^{d-1} dr$

$\Rightarrow$ generalized to d-dimensions,

$$b_2 = \frac{S_d}{2v_\alpha}\left(\int r^{d-1} dr \left(e^{-\beta u(r)} - 1\right)\right)$$

$$S_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}$$

$$b_2 = \frac{S_d}{2V_\alpha}\left(\int r^{d-1}dr\left(e^{-\beta u(r)}-1\right)\right)$$

*Now use $u(r) = \begin{cases} \infty & r<a \\ -u_0 & a<r<b \\ 0 & r>b \end{cases}$

$$= \frac{S_d}{2V_\alpha}\left[\int_0^a r^{d-1}dr\left(\cancel{e^{-\beta\infty}}^{\,0}-1\right) + \int_a^b r^{d-1}dr\left(e^{\beta u_0}-1\right)\right]$$

$$\boxed{b_2 = \frac{S_d}{2V_\alpha}\left[-\frac{a^d}{d} + \left(e^{\beta u_0}-1\right)\frac{b^d-a^d}{d}\right]}$$

where $S_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}$ and $V_\alpha = l_\alpha^d$

<u>high T limit</u>: $e^{\beta u_0} \simeq 1+\beta u_0$

$$\Rightarrow b_2 \to \frac{S_d}{2V_\alpha}\left[-\frac{a^d}{d} + \beta u_0\frac{b^d-a^d}{d}\right]$$

<u>low T</u>: $b_2 \to \frac{S_d}{2V_\alpha} e^{\beta u_0}\frac{b^d-a^d}{d}$

b.) Calculate $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,N}$

* Use $\frac{PV}{N k_B T} = 1 + a_2 \frac{v_\alpha}{v} + \cdots$ (L 26 notes)

and $a_2 = -b_2$

$$\therefore \frac{P}{k_B T} = \frac{N}{V} - \left(\frac{N}{V}\right)^2 v_\alpha b_2 .$$

at constant N & T:

$$\therefore \frac{dP}{k_B T} = -\frac{N}{V^2} dV + 2\left(\frac{N}{V}\right)^2 \frac{1}{V} v_\alpha b_2 \, dV$$

$$\Rightarrow \frac{\partial V}{\partial P}\Big|_{T,N} = \frac{1}{k_B T} \cdot \frac{1}{-\frac{N}{V^2} + 2\left(\frac{N}{V}\right)^2 \frac{1}{V} v_\alpha b_2}$$

$$= \frac{V}{k_B T} \frac{1}{-\left(\frac{N}{V}\right) + 2\left(\frac{N}{V}\right)^2 v_\alpha b_2}$$

$$= -\frac{V^2}{N k_B T} \cdot \frac{1}{1 - 2 n v_\alpha b_2}$$

$$\boxed{\therefore \kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = \frac{V}{N k_B T} \frac{1}{1 - 2 n v_\alpha b_2} \overset{n \text{ small}}{\approx} \frac{V}{N(k_B T)}\left(1 + 2 n v_\alpha b_2\right)}$$

c.) high T VdW parameters

from L26, VdW EOS has (setting $k_B = 1$)

$$P = \frac{T}{v - b_{vdw}} - \frac{a_{vdw}}{v^2}$$

where we attached "vdw" to a + b to avoid confusion with the a + b that appear in the def. of $u(r)$.

In our present case,

$$P = \frac{N}{V}T - \left(\frac{N}{V}\right)^2 v_Q \, b_2 T.$$

$$b_2 \xrightarrow[T \gg 1]{} \frac{S_d}{2 v_Q}\left[-\frac{a^d}{d} + \beta u_0 \frac{b^d - a^d}{d}\right]$$

$$P = \frac{T}{v} - \frac{v_Q}{v^2}\frac{T}{2 v_Q}\left[-\frac{S_d a^d}{d} + \frac{u_0}{T}\frac{S_d (b^d - a^d)}{d}\right]$$

* use now $V_d(a) = \frac{S_d a^d}{d}$ = d-dim vol. in radius a

$V_d(b) = \frac{S_d b^d}{d}$ = " " radius b

$$\Rightarrow P = \frac{T}{v} - \frac{T}{2v^2}\left[-V_d(a) + \frac{u_0}{T}\left(V_d(b) - V_d(a)\right)\right]$$

$$, P = \frac{T}{v} - \frac{T}{2v^2}\left[-V_d(a) + \frac{\mu_0}{T}\left(V_d(b) - V_d(a)\right)\right]$$

$$= T\left[\frac{1}{v} + \frac{V_d(a)}{2v^2}\right] - \frac{\mu_0}{2v^2}\left(V_d(b) - V_d(a)\right)$$

$$= \frac{T}{v}\left[1 + \frac{V_d(a)}{2v}\right] - \frac{\mu_0}{2v^2}\left(V_d(b) - V_d(a)\right)$$

* Now use since $v \gg 1$,

$$\frac{1}{1 - \frac{V_d(a)}{2v}} \simeq 1 + \frac{V_d(a)}{2v}$$

$$\Rightarrow P \simeq \frac{T}{v}\frac{1}{1 - \frac{V_d(a)}{2v}} - \frac{\mu_0}{2v^2}\left(V_d(b) - V_d(a)\right)$$

$$= \frac{T}{v - \frac{V_d(a)}{2}} - \frac{\mu_0}{2v^2}\left(V_d(b) - V_d(a)\right)$$

Comparing to $P = \dfrac{T}{v - b_{vdw}} - \dfrac{a_{vdw}}{v^2}$

$$\Rightarrow \boxed{\begin{aligned} b_{vdw} &= \frac{V_d(a)}{2} = \frac{S_d a^d}{2d} = \frac{2\pi^{d/2}}{\Gamma(\frac{d}{2})}\frac{a^d}{2d} \\ a_{vdw} &= \frac{1}{2}\mu_0\left(V_d(b) - V_d(a)\right) \end{aligned}}$$

d.) $d=1$ calculation of b_3 for $u(r) = \infty \quad r<a$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 0 \quad r>a$

$$b_3 = \frac{1}{6\lambda_a^2 V}\left(Q_3 - 3Q_1Q_2 + 2Q_1^3\right)$$

Now, $$Q_3 = \iiint dr_1\,dr_2\,dr_3\; e^{-\beta u_{12}} e^{-\beta u_{13}} e^{-\beta u_{23}}$$

$$= \iiint dr_1\,dr_2\,dr_3\;(1+f_{12})(1+f_{13})(1+f_{23})$$

$$f_{ij} = e^{-\beta u_{ij}} - 1$$

<u>Note</u> $$f(\vec{r}_i - \vec{r}_j) = \begin{cases} -1 & r_{ij} < a \\ 0 & r_{ij} > a \end{cases}$$

$$\Rightarrow Q_3 = \iiint dr_1\,dr_2\,dr_3\,\left(1 + f_{12} + f_{13} + f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{23}f_{13} + f_{12}f_{13}f_{23}\right)$$

$$Q_3 = \iiint dr_1\,dr_2\,dr_3\,\left(1 + 3f_{12} + 3f_{12}f_{23} + f_{12}f_{13}f_{23}\right)$$

* Call $\int dr_1 = V$ etc. (even though we're in $d=1$)

$$Q_3 = V^3 + 3V\iint dr_1\,dr_2\,f_{12} + 3\iiint dr_1\,dr_2\,dr_3\,f_{12}f_{23} + \iiint dr_1\,dr_2\,dr_3\,f_{12}f_{13}f_{23}$$

use $\iint dr_1 dr_2\, f_{12} = \int dR \int dr\, f(r)$ $\quad R = \frac{r_1+r_2}{2}$

$r = r_1 - r_2$

recall $f(r) = -1$ for $|r| < a$

$= 0$ else

$$\Rightarrow \iint dr_1 dr_2 f_{12} = V \int_{-a}^{a} (-1)\, dr = -2aV$$

$$\boxed{\therefore Q_3 = V^3 - 6aV^2 + 3\iiint dr_1 dr_2 dr_3\, f_{12} f_{23} + \iiint dr_1 dr_2 dr_3\, f_{12} f_{23} f_{13}}$$

come back to this shortly... first we show the 1st 2 terms in Q_3 are cancelled!

$$Q_2 = \iint dr_1 dr_2 (1+f_{12}) = V^2 - 2aV$$

$$Q_1 = \int dr_1 = V$$

$$\Downarrow$$

$$\therefore Q_3 - 3Q_1Q_2 + 2Q_1^3 = \cancel{V^3} - \cancel{6aV^2} + 3\iiint f_{12}f_{23} + \iiint f_{12}f_{13}f_{23} - \cancel{3V^3} + \cancel{6aV^2} + \cancel{2V^3}$$

$$\Rightarrow b_3 = \frac{1}{6v_Q^2 V}\left[3\iiint dr_1 dr_2 dr_3\, f_{12} f_{23} + \iiint dr_1 dr_2 dr_3\, f_{12} f_{13} f_{23}\right]$$

let $\Omega_1 = r_1$
$\Omega_2 = r_2 - r_1$
$\Omega_3 = r_3 - r_2$

$$\Rightarrow \iiint dr_1 dr_2 dr_3 \, f_{12} f_{23}$$
$$= \iiint d\Omega_1 d\Omega_2 d\Omega_3 \, f(\Omega_2) f(\Omega_3)$$
$$= V(-2a)^2$$

$$\boxed{\iiint dr_1 dr_2 dr_3 f_{12} f_{23} = 4a^2 V}$$

* <u>For the term w/ 3 f's</u>

$$\iiint dr_1 dr_2 dr \; f(r_1 - r_2) f(r_2 - r_3) f(r_3 - r_1)$$

I simply plug into Mathematica

$$(-1)^3 \int_{-L}^{L}\int_{-L}^{L}\int_{-L}^{L} dr_1 dr_2 dr_3 \; \theta(a - |r_1 - r_2|)\theta(a - |r_2 - r_3|) \theta(a - |r_1 - r_3|)$$

$$= 2a^2(a - 3L)$$

<u>Note</u>: $V = \int_{-L}^{L} dr = 2L$ and it's ok to assume $L >> a$

$$\boxed{\iiint fff \approx -6a^2 L = -3a^2 V}$$

$\therefore$ adding up all terms

$$\Rightarrow \; b_3 = \frac{1}{6 v_\alpha^2 \cancel{\gamma}} 9a^2 \cancel{\gamma}$$

$$\boxed{b_3 = \frac{3a^2}{2 v_\alpha^2}}$$

where here,
$v_\alpha = l_\alpha$ since
in 1d.

Sorry, that was a bit more tedious than I thought it would be!!