admin reminders

1) Final exam (Subject exam) Friday 12/17 7:45-10:45 am
2) Midterm 2 will be a take home exam (after TG break)
3) HW 7 posted later today due next Wed. 11/24

Recap from Monday's activity sheet

* New (brief) topic - approximate methods to deal with interacting particles/DOF

* So far, we've only treated non-interacting systems (ideal gases, paramagnets, einstein/debye solids, blackbody radiation, etc.)

* While this has its uses - i.e, many problems in Solid State, nuclear, molecular/atomic, astrophy. systems can be modelled as non-interacting in 1st approximation - a wide range of interesting phenomena (collective/emergent phenomena like superfluidity/superconductivity, phase transitions, etc.) arise from interactions between particles & cannot be understood without including their effects on SM/TD properties.

* Simple methods (Perturbative/Variational) ~ 3 classes

* Sophisticated methods (Renormalization group/ theory of phase transitions) ~ 6-7 classes

Perturbative Methods

$$H = \underset{\text{easy}}{H_0} + \underset{\text{hard}}{V}$$

* Schematically, let $H = H_0 + V$

$$Z = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\, e^{-\beta H_0} e^{-\beta V}$$

$$= \frac{\mathrm{Tr}\, e^{-\beta H_0} e^{-\beta V}}{\mathrm{Tr}\, e^{-\beta H_0}} \mathrm{Tr}\, e^{-\beta H_0}$$

$$= \frac{1}{Z_0} \mathrm{Tr}\, e^{-\beta H_0} e^{-\beta V} \, Z_0$$

$$= \langle e^{-\beta V} \rangle_0 Z_0$$

* If V is "small," then expect

$$e^{-\beta V} = 1 + \underbrace{e^{-\beta V} - 1}_{\text{"small"}}$$

$$\therefore \; Z = \langle 1 \rangle_0 Z_0 + \langle e^{-\beta V} - 1 \rangle_0 Z_0$$

or

$$\left(\frac{Z}{Z_0}\right) = 1 + \langle e^{-\beta V} - 1 \rangle_0$$

$$= 1 + \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} \langle V^n \rangle_0$$

Virial Cluster expansion

* apply the perturbative treatment of V to the classical gas

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \underbrace{\sum_{i<j} u(|\vec{r}_i - \vec{r}_j|)}_{\equiv\, U}$$

* Physical idea: high T + low density
  $\Rightarrow$ KE dominates over U
  $\Rightarrow$ expect ideal gas-like properties + small corrections (get bigger as T↓ and n↑)

* Work in the Grand Canonical Ensemble

$$\mathcal{Z} = \sum_{N=0}^{\infty} \underset{\text{Gibbs factor}}{\frac{1}{N!}} \int \frac{d^{3N}\vec{r}\, d^{3N}p}{(2\pi\hbar)^{3N}}\, e^{-\beta\left(\sum_{i=1}^{N}\frac{p_i^2}{2m} + \sum_{i<j} u(\vec{r}_{ij}) - \mu N\right)}$$

$$= \sum_{N=0}^{\infty} \left(e^{\beta\mu}\right)^N \underbrace{\frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^{3N}}\, e^{-\beta\sum_i \frac{p_i^2}{2m}}}_{\frac{1}{N!}\frac{3^N}{l_Q^{3N}}} \int d^{3N}r\, e^{-\beta U}$$

$$l_Q = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$$

df. "Configuration integral"

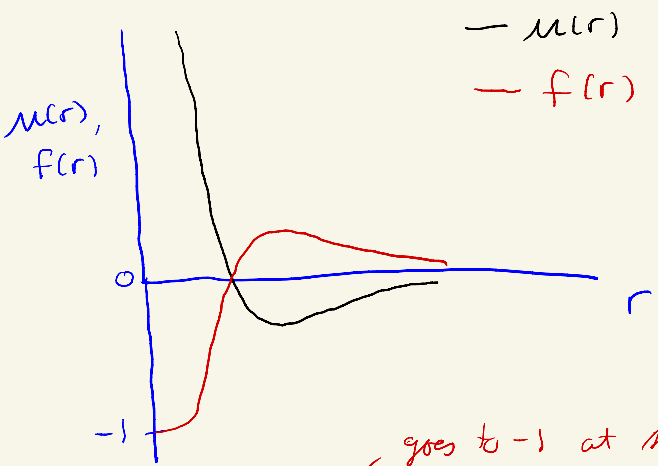
$$\boxed{\begin{aligned} Q_N &\equiv \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \, e^{-\beta \sum_{i<j} u(|\vec{r}_i - \vec{r}_j|)} \\ &= \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \prod_{i<j} e^{-\beta u(|\vec{r}_{ij}|)} \end{aligned}}$$

Contains all the non-trivial physics!

Aside on how to approximate Q_N

* let $e^{-\beta u_{ij}} = 1 + (e^{-\beta u_{ij}} - 1) \equiv 1 + f_{ij}$

typically, the form of $u(|\vec{r}_{ij}|)$ looks like



goes to -1 at small r

* f(r) convenient

bounded + goes to zero large r

$$\therefore\ Q_N = \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \prod_{i<j} (1+f_{ij})$$

$$= \int d^3 r_1 \cdots d^3\vec{r}_N \left(1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j \\ k<l}} f_{ij} f_{kl} + \cdots \right)$$

* Becomes very tedious/complicated ⇒ See the text for the Mayer cluster expansion method that uses diagrammatic techniques to organize this. (Intuitively, terms w/ more f's are subleading)

$$\Downarrow$$

The result of a very long/technical development is that

$$\frac{PV}{TN} = \frac{\log Z}{N} = \sum_{m=1}^{\infty} a_m(T) \left(\frac{v_Q}{v}\right)^{m-1}$$

let $v = \frac{V}{N} = \frac{1}{n}$

$$\Rightarrow \boxed{\frac{Pv}{T} = \sum_{m=1}^{\infty} a_m(T) \left(\frac{v_Q}{v}\right)^{m-1} \qquad v_Q = l_Q^3 = \left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}}$$

* Does it make sense? ① Ideal gas $\frac{Pv}{T} = 1$ is the leading term ($m=1$) ✓

② corrections grow as n increases ($v\downarrow$) ✓

③ " " as T decreases ($v_Q \uparrow$) ✓

* How to actually calculate $a_m(T)$?

$$Z = \sum_{N=0}^{\infty} \frac{z^N}{N!\, v_Q^N} Q_N$$

$$\equiv \sum_{N=0}^{\infty} C_N z^N \qquad C_N \equiv \frac{Q_N}{N!\, v_Q^N}$$

(Power series in z, Recall $z \ll 1$ for high T / low n)

* Since $\frac{Pv}{T} = \frac{1}{N} \log Z = \sum_{m=1}^{\infty} a_m(T) \left(\frac{v_Q}{v}\right)^{m-1}$, let's develop a power series in z for $\log Z$

$$\log Z = \log\left(1 + \sum_{N=1}^{\infty} C_N z^N\right)$$ high T, low $n \Rightarrow z \ll 1$

$$\therefore \log Z = \log(1 + \mathcal{E}(z))$$

where $\mathcal{E}(z) = \sum_{N=1}^{\infty} C_N z^N$

Now use: $\log(1+\mathcal{E}) = \mathcal{E} - \frac{\mathcal{E}^2}{2} + \frac{\mathcal{E}^3}{3} + \cdots$

* Let's just calculate terms thru $\mathcal{O}(z^3)$ to get our bearings (higher terms are subleading)

$$\log Z \simeq \left(c_1 z + c_2 z^2 + c_3 z^3\right) - \frac{1}{2}\left(c_1 z + c_2 z^2 + c_3 z^3\right)^2$$

$$+ \frac{\left(c_1 z + c_2 z^3 + c_3 z^3\right)^3}{3}$$

* Since we only care about terms through $\mathcal{O}(z^3)$,

$$\Rightarrow \log Z \simeq c_1 z$$

$$+ z^2\left(c_2 - \frac{1}{2}c_1^2\right)$$

$$+ z^3\left(c_3 - c_1 c_2 + \frac{c_1^3}{3}\right)$$

$\therefore$ If $\log Z = \sum_{m=1}^{\infty} B_m z^m$

$$B_1 = c_1 = \frac{Q_1}{v_Q}$$

$$B_2 = c_2 - \frac{1}{2}c_1^2 = \frac{Q_2}{2!\, v_Q^2} - \frac{Q_1^2}{2 v_Q^2} = \frac{1}{2 v_Q^2}\left(Q_2 - Q_1^2\right)$$

$$B_3 = c_3 - c_1 c_2 + \frac{c_1^3}{3} = \frac{Q_3}{6 \cdot v_Q^3} - \frac{Q_1 Q_2}{2 v_Q^3} + \frac{Q_1^3}{3 v_Q^3}$$

$$= \frac{1}{6 v_Q^3}\left(Q_3 - 3 Q_1 Q_2 + 2 Q_1^3\right)$$

* It's conventional to write

$$\log \mathcal{Z} = \frac{V}{v_Q} \sum_{m=1}^{\infty} b_m(T,V)\, z^m$$

(i.e., $b_m = \frac{v_Q}{V} B_m$)

$$\therefore \; b_1(T,V) = \frac{Q_1}{V}$$

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

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

$$\vdots$$

* This is still not what we want, since it's an expansion in z. What we really want is an expansion in $\frac{N}{V}$ (or inverse powers of $v = \frac{V}{N}$)

* To do this, we need to relate N + z + basically invert to get $z = z(N)$

$$N = T \frac{\partial}{\partial \mu} \log Z \Big|_T$$

but $\frac{\partial}{\partial \mu}(\ )_T = \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z}(\ )_T$ $\qquad z = e^{\mu/T}$

$$\frac{\partial z}{\partial \mu} = \frac{1}{T} z$$

$$\therefore N = z \frac{\partial}{\partial z} \log Z \Big|_T$$

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

$$\boxed{N = \frac{V}{v_Q} \sum_{m=1}^{\infty} m\, b_m z^m} \quad (A)$$

and

$$\boxed{\log Z = \frac{V}{v_Q} \sum_{m=1}^{\infty} b_m z^m} \quad (B)$$

$$(A) \Rightarrow \boxed{\frac{N}{V} v_Q = \left(\frac{v_Q}{v}\right) = \sum_{m=1} m\, b_m z^m} \quad (A)'$$

$(B) \Rightarrow \frac{PV}{T} = \frac{V}{v_Q} \sum_m b_m z^m \Rightarrow$ divide both sides by N

$$\Rightarrow \boxed{\frac{Pv}{T} = \frac{v}{v_Q} \sum_m b_m z^m = \sum_{m=1} a_m(T) \left(\frac{v}{v_Q}\right)^{m-1}}$$

* Now combine Ⓐ' + Ⓑ' to relate a_m + b_m:

$$\frac{pv}{T} = \sum_{m=1}^{\infty} a_m \left(\frac{v_\alpha}{v}\right)^{m-1} \overset{Ⓐ'}{=} \sum_m a_m \left(\sum_n n b_n z^n\right)^{m-1} \quad Ⓒ$$

but
$$\frac{pv}{T} = \frac{v}{v_\alpha} \sum_{m=1}^{\infty} b_m z^m \overset{Ⓐ'}{=} \frac{\sum_m b_m z^m}{\sum_m m b_m z^m} \quad Ⓓ$$

* Setting Ⓒ = Ⓓ + equating coefficients of like powers of z

e.g. $Ⓒ = a_1 + a_2(b_1 z + 2b_2 z^2 + 3b_3 z^3) +$
$a_3(b_1 z + 2b_2 z^2 + \cdots)^2$

$$\boxed{Ⓒ = a_1 + z(a_2 b_1) + z^2(2b_2 a_2 + b_1^2 a_3) + z^3(3b_3 a_2 + 4 b_2 b_1 a_3)}$$

$$Ⓓ = \frac{b_1 z + b_2 z^2 + b_3 z^3 \cdots}{b_1 z + 2b_2 z^2 + 3b_3 z^3 \cdots}$$

$$= 1 - \frac{b_2}{b_1} z + \frac{2(b_2^2 - b_1 b_3)}{b_1^2} z^2 \cdots$$

$$\Rightarrow \boxed{a_1 = 1 = b_1 \, ; \; a_2 = -b_2 \, ; \; a_3 = 4b_2 - 2b_3 \quad \text{etc}}$$

* Will usually content ourselves to stop at a_2

$$a_2 = -b_2 = -\frac{1}{2v_Q V}\left(Q_2 - Q_1^2\right)$$

$$Q_1 = V$$

$$Q_2 = \int d^3r_1\, d^3r_2\; e^{-\beta u(\vec{r}_{12})}$$

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

$$\Rightarrow Q_2 = \int d^3\vec{R} \int d^3\vec{r}\; e^{-\beta u(r)} = 4\pi V \int r^2 dr\; e^{-\beta u(r)}$$

$$\boxed{\therefore\; a_2 = -\frac{2\pi}{v_Q}\int_0^\infty r^2 dr\left(e^{-\beta u(r)} - 1\right)}$$

$$\Downarrow$$

$$\boxed{\frac{Pv}{T} = 1 - \frac{2\pi N}{V}\int_0^\infty r^2 dr\left(e^{-\beta u(r)} - 1\right)}$$

1st order Virial EOS

e.g. Van der Waals gas EOS

$$u(r) = \begin{cases} \infty & r < r_0 \\ -u_0\left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases}$$

"Lennard-Jones potential"

$$a_2 = -\frac{2\pi}{v_Q}\int_0^\infty r^2 dr\left(e^{-\beta u(r)} - 1\right)$$

$$= \frac{-2\pi}{v_Q}\left[-\int_0^{r_0} r^2 dr + \int_{r_0}^\infty r^2 dr\left(e^{-\frac{\beta u_0 r_0^6}{r^6}} - 1\right)\right]$$

for $T \gg u_0$ $\quad e^{-\beta u(r)} \simeq 1 - \beta u(r)$

$$\Rightarrow \boxed{a_2 \simeq \frac{2\pi r_0^3}{3 v_Q}\left(1 - \frac{u_0}{T}\right)}$$

EOS: $\frac{Pv}{T} = 1 + \frac{2\pi r_0^3}{3v}\left(1 - u_0/T\right)$ $\quad$ * let $b = \frac{2\pi r_0^3}{3}$

$a = b u_0$

$$\Rightarrow P = \frac{T}{v} + \frac{bT}{v^2} - \frac{a}{v^2} \simeq \frac{T}{v-b} - \frac{a}{v^2}$$