Reminders

1. Final exam Friday 12/17 7:45 am
2. Midterm 2 (take home) after TG break
3. HW 7 due Weds before TG break

Recap

* Techniques to handle interacting systems

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high T, low n <u>Virial Cluster expansion</u>

$$\boxed{\frac{Pv}{T} = \sum_{m=1}^{\infty} a_m(T)\left(\frac{v_\alpha}{v}\right)^{m-1} \qquad \left(v = \frac{1}{n} = \frac{V}{N} \quad v_\alpha = l_\alpha^3 = \left(\frac{\hbar^2 2\pi}{m k_B T}\right)^{3/2}\right)}$$

Classical gas

$$Z = \sum_{N=0}^{\infty} C_N z^N \qquad C_N = \frac{Q_N}{N!\, v_\alpha^N} \qquad z = e^{\beta\mu}$$

$(z \ll 1$ high T, low n$)$

$$Q_N = \int d\vec{r}_1 \cdots d\vec{r}_N \, e^{-\beta \sum_{i<j} u(\vec{r}_i - \vec{r}_j)}$$

"Config. Integral"

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

$$b_1 = \frac{v_Q}{V} C_1$$

$$b_2 = \frac{v_Q}{V}\left(C_2 - \tfrac{1}{2} C_1^2\right)$$

etc...

$$\boxed{N = z \frac{\partial}{\partial z} \log Z \Big|_T = \frac{V}{v_Q} \sum_{m=1}^{\infty} m b_m z^m}$$ (B)

* Combined (A) + (B) to get calculable expressions for $a_m(T)$

$$a_1 = b_1 = 1$$

$$a_2 = -b_2 = -\frac{v_Q}{V}\left(C_2 - \tfrac{1}{2} C_1^2\right) = -\frac{1}{2 v_Q V}\left(Q_2 - Q_1^2\right)$$

etc...

<u>Main point</u>: the a_m given by closed form integrals over the $e^{-\beta u_{ij}}$ factors, though they become complicated in general for $m \gtrsim 3$

Quantum Virial Coefficients

* Pathria + Beale go thru the formal development of QM generalizations of the cluster expansions that led to the virial coefficients previously.

* Here, I'll be <u>much</u> less formal + give a heuristic discussion + show how to calculate b_2 for identical interacting fermions or bosons

as before, we have from the def. of the GCE:

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\alpha} e^{-\beta(E_\alpha^N - \mu N)}$$

$$= \sum_{N=0}^{\infty} z^N Z_N \qquad Z_N = \sum_{\alpha} e^{-\beta E_\alpha^N} ; \; z = e^{\beta\mu}$$

$$\boxed{\mathcal{Z} = 1 + \sum_{N=1}^{\infty} z^N Z_N}$$

* as before, we take $\log \mathcal{Z} = \log(1+\varepsilon)$ where $\varepsilon = \sum_{N=1}^{\infty} z^N Z_N$ + Taylor expand to find

$$\log \mathcal{Z} \simeq z Z_1 + z^2\left(Z_2 - \tfrac{1}{2} Z_1^2\right) + \cdots$$

$$\boxed{\begin{aligned} &\therefore \text{ defining } \log \mathcal{Z} \equiv \frac{V}{v_Q} \sum_{m=1}^{\infty} b_m z^m \\ &\Rightarrow b_1 = \frac{v_Q}{V} Z_1 , \quad b_2 = \frac{v_Q}{V}\left(Z_2 - \tfrac{1}{2} Z_1^2\right) \text{ etc} \end{aligned}}$$

* For simplicity, we'll assume spinless bosons/fermions (of course, fermions can't have $S=0$. But we can imagine we are dealing with a gas of spin-polarized particles where, say, all particles are in the $S_z = \uparrow$ state, & the $v(\vec{r}_{ij})$ doesn't "flip" spins)

$$Z_1 = \sum_{\vec{p}} e^{-\beta\frac{p^2}{2m}} \longrightarrow V\int\frac{d^3p}{(2\pi\hbar)^3}\, e^{-\beta\frac{p^2}{2m}}$$

$$\boxed{Z_1 = \frac{V}{\ell_Q^3} \quad \text{as before} \quad \left(\ell_Q = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}\right)}$$

* How to get Z_2?

$$Z_2 = \sum_n e^{-\beta E_n^{N=2}}$$

$$\hat{H}_{N=2} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + u(|\vec{r}_1 - \vec{r}_2|)$$

let $\vec{P} = \vec{P}_1 + \vec{P}_2$

$\vec{p} = \frac{1}{2}(\vec{P}_1 - \vec{p}_2)$

$\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$

$\vec{r} = (\vec{r}_1 - \vec{r}_2)$

$$\Rightarrow \hat{H}_{N=2} = \underbrace{\frac{P^2}{4m}}_{\text{com coord only}} + \underbrace{\frac{p^2}{m} + u(r)}_{\text{relative coords. only}}$$

$\therefore$ Sch. Eqn for $N=2$ becomes

$$\left[-\frac{\hbar^2\vec{\nabla}_R^2}{4m} - \frac{\hbar^2}{m}\vec{\nabla}_r^2 + u(r)\right]\Psi_n(\vec{R},\vec{r}) = E_n\,\Psi_n(\vec{R},\vec{r})$$

$$\Rightarrow \Psi_n(\vec{R},\vec{r}) = e^{i\vec{P}\cdot\vec{R}}\,\psi_n(\vec{r})$$

free particle motion for COM

relative motion + all non-trivial effects from $u(r)$.

$\Rightarrow$ relative coord Sch. Eqn

$$\boxed{\left(-\frac{\hbar^2\nabla_r^2}{m} + u(r)\right)\psi_n(\vec{r}) = \epsilon_n\,\psi_n(\vec{r}) \quad \text{and} \quad E_{n,p} = \frac{P^2}{4m} + \epsilon_n}$$

* Depending on the nature of $u(r)$, we can have

ϵ_n — discrete bound state $\epsilon_n < 0$

and/or

continuum $\epsilon_n > 0$ $\quad \epsilon_n = \frac{p^2}{m}$

relative momentum

OK. So we have

$$Z_2 = \sum_{\vec{P}, n} e^{-\beta\left(\frac{P^2}{4m} + \epsilon_n\right)}$$

* Assuming ϵ_n has both discrete BS & continuum scattering states

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$$Z_2 = \underbrace{\sum_{\vec{P}, n} e^{-\frac{\beta P^2}{4m}} e^{-\beta \epsilon_n}}_{\substack{\text{discrete BS.} \\ \epsilon_n < 0 \text{ terms}}} + \underbrace{\sum_{\vec{P}} e^{-\frac{\beta P^2}{4m}} \int_0^\infty d\epsilon \, g(\epsilon) \, e^{-\beta \epsilon}}_{\substack{\text{continuum } \epsilon_n = \epsilon > 0 \\ \text{w/ DOS } g(\epsilon)}}$$

* Now, use that

$$\sum_{\vec{P}} e^{-\frac{\beta P^2}{4m}} = V \int \frac{d^3P}{(2\pi\hbar)^3} e^{-\frac{\beta P^2}{4m}}$$

$$= \frac{V}{\ell_Q^3(2m)} = \frac{V}{v_Q(2m)}$$

i.e., recall that for a particle of mass m $\ell_Q = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$ depends on m, so for COM motion $m \to 2m$.

$$\boxed{\therefore Z_2 = \frac{V}{v_Q(2m)} \left(\sum_n e^{-\beta \epsilon_n} + \int d\epsilon \, e^{-\beta\epsilon} g(\epsilon) \right) \equiv \frac{V}{v_Q(2m)} Z_{2,\text{rel}}}$$

$$\therefore \; b_2 = \frac{v_Q(m)}{V}\left(Z_2 - \frac{1}{2} Z_1^2 \right)$$

* Recall, (see HW7 + also ~ lectures 17-19) that even for <u>non-interacting</u> fermi/bose gases, there is a correction to non-ideal gas behavior for high T/low n that has the form of a virial coefficient

i.e.,
$$b_2^0 = \frac{v_Q(m)}{V}\left(Z_2^0 - \frac{1}{2} Z_1^2 \right) = \pm 2^{-5/2}$$

Boson ($+$), Fermi ($-$)

Z_2^0: Z_2 w/ $u(r) = 0$

* what we want is an expression for $b_2 - b_2^0$ since that isolates the effects of $u(r)$

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$$b_2 - b_2^0 = \frac{v_Q(m)}{V}\left(Z_2 - Z_2^0 \right)$$

$$= \frac{v_Q(m)}{\cancel{V}} \frac{\cancel{V}}{v_Q(2m)} \left[\sum_n e^{-\beta \epsilon_n} + \int d\epsilon \, e^{-\beta\epsilon} \left(g(\epsilon) - g^0(\epsilon) \right) \right]$$

$$\boxed{b_2 - b_2^0 = 2^{3/2} \left[\sum_n e^{-\beta \epsilon_n} + \int d\epsilon \, e^{-\beta\epsilon} \left(g(\epsilon) - g^0(\epsilon) \right) \right]}$$

Now, continuum $\epsilon = \frac{\hbar^2 k^2}{m}$ for both the interacting + non-interacting systems. Only the density of states $g(\epsilon)$ + $g^0(\epsilon)$ differs

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here, we follow convention + use DOS wrt k $\tilde{g}(k)$ (rather than ϵ) to write

$$\boxed{b_2 - b_2^0 = 2^{3/2}\left[\sum_n e^{-\beta\epsilon_n} + \int dk\, e^{-\beta\frac{\hbar^2 k^2}{m}}\left(\tilde{g}(k) - \tilde{g}^0(k)\right)\right]}$$

How to get $\tilde{g}(k) - \tilde{g}^0(k)$? Use an ingenious trick due to Beth + Uhlenbeck (1937) to write it in terms of 2-body scattering phase shifts $\delta_\ell(k)$

[I am brief here assuming you've had at least some scattering theory in your previous/current QM courses]

* Since $u(r)$ has no angular dependence, the Sch. eqn. is separable in (r, θ, ϕ)

$$\Rightarrow \boxed{\begin{aligned} \psi_{k\ell m}(r,\theta,\phi) &= A_{k\ell m}\, Y_{\ell m}(\theta,\phi)\, \frac{u_{k\ell}(r)}{r} \\ \psi^{(0)}_{k\ell m}(r,\theta,\phi) &= A^{(0)}_{k\ell m}\, Y_{\ell m}(\theta,\phi)\, \frac{u^{(0)}_{k\ell}(r)}{r} \end{aligned}}$$

Fermions $\Psi(-\vec{r}) = -\Psi(\vec{r})$
Bosons $\Psi(-\vec{r}) = +\Psi(\vec{r})$

$\Big\}$ $l = 0, 2, 4, \ldots$ bosons
$= 1, 3, 5, \ldots$ fermion

Boundary conditions

* Take the container to be a spherical cavity of radius R that will let go to ∞ @ the end

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$$\text{X} \quad \boxed{u_{kl}(R) = u_{kl}^{(0)}(R) = 0}$$

(hard wall BC)

* Now, well outside the range of $u(r)$ (i.e., where $u(r) \to 0$), we know

1.) $u_{kl}(r) \xrightarrow{r\to\infty} \sin\left[kr + \frac{l\pi}{2} + \delta_l(k)\right]$

2.) $u_{kl}^{(0)}(r) \longrightarrow \sin\left[kr + \frac{l\pi}{2}\right]$

* The allowed/quantized values of k from X

1.) $\sin\left(kR + \frac{l\pi}{2} + \delta_l(k)\right) = 0 \implies kR + \frac{l\pi}{2} + \delta_l(k) = n\pi$
(interacting case)

2.) $\sin\left(kR + \frac{l\pi}{2}\right) = 0 \implies kR = n\pi$
(free case)

Note: each eigenvalue k for given l is $(2l+1)$-fold degenerate

* For fixed l, changing $\Delta n = 1$ gives a change Δk as

$$kR + \frac{l\pi}{2} + \delta_l(k) = \pi n \qquad (1)$$

$$(k+\Delta k)R + \frac{l\pi}{2} + \delta_l(k+\Delta k) = \pi(n+1) \qquad (2)$$

$$(2)-(1) = \Delta k R + \underbrace{\delta_l(k+\Delta k) - \delta_l(k)}_{\approx \frac{\partial \delta_l}{\partial k}\Delta k} = \pi$$

$$\therefore \boxed{\Delta k = \frac{\pi}{R + \frac{\partial \delta_l}{\partial k}} \qquad \text{interacting case}}$$

* Similarly, for the non-interacting case

$$\boxed{\Delta k^{(0)} = \frac{\pi}{R}}$$

These are the spacings of quantized k's for given l.

*Let $\tilde{g}_\ell(k)\,dk$ = # of states of fixed ℓ lying between k + $k+dk$

$\therefore$ Require

$$\boxed{\begin{aligned} \tilde{g}_\ell(k)\,\Delta k &= 2\ell+1 \\ \tilde{g}_\ell^{(0)}(k)\,\Delta k^{(0)} &= 2\ell+1 \end{aligned}}$$

plugging in previous expressions for Δk + $\Delta k^{(0)}$

$$\Rightarrow \tilde{g}_\ell(k) = \frac{2\ell+1}{\pi}\left[R + \frac{\partial \delta_\ell}{\partial k}\right]$$

$$\Rightarrow \tilde{g}_\ell^{(0)}(k) = \frac{2\ell+1}{\pi} R$$

$$\therefore \boxed{\tilde{g}_\ell(k) - \tilde{g}_\ell^{(0)}(k) = \frac{2\ell+1}{\pi}\frac{\partial \delta_\ell(k)}{\partial k}}$$

* Coming back to our desired formula for

$$b_2 - b_2^0 = 2^{3/2}\Big[\sum_n e^{-\beta E_n} + \underbrace{\int dk\, e^{-\beta\frac{\hbar^2 k^2}{m}}\left(\tilde{g}(k) - \tilde{g}^0(k)\right)}\Big]$$

$$\| $$

$l = 0, 2, 4, \ldots$ Bosons $\rightarrow$
$= 1, 3, 5, \ldots$ Fermions

$$\sum_l{}' \int dk\, e^{-\beta\frac{\hbar^2 k^2}{m}}\left(\tilde{g}_l(k) - \tilde{g}_l^{(0)}(k)\right)$$

$$\therefore\ \boxed{\begin{aligned} b_2 - b_2^{(0)} &= 2^{3/2}\Big\{\sum_n e^{-\beta E_n} + \frac{1}{\pi}\int_0^\infty dk \sum_l{}'(2l+1)\frac{\partial \delta_l}{\partial k}\, e^{-\beta\frac{\hbar^2 k^2}{m}}\Big\} \\ &= 2^{3/2}\Big\{\sum_n e^{-\beta E_n} + \frac{l_\alpha^2}{\pi^2}\int_0^\infty k\,dk \sum_l{}'(2l+1)\,\delta_l(k)\, e^{-\beta\frac{\hbar^2 k^2}{m}}\Big\}\end{aligned}}$$

"Beth Uhlenbeck formula"

Remarks: 1.) Unlike Classical case, only b_2 has closed form expression

2) For a sharp resonance, $\delta(k)$ increases by π over small interval in energy

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$$\frac{\partial \delta_l}{\partial k} \approx \pi\, \delta_l(k - k_0) \qquad k_0 = \text{center of resonance}$$

$\Rightarrow$ resonance acts like a B.S. in contribution to b_2

since

$$\frac{1}{\pi}\int dk\,(2\ell+1)\,\frac{\partial \delta_\ell}{\partial k}\,e^{-\frac{\beta\hbar^2 k^2}{m}}$$

$$\longrightarrow e^{-\frac{\beta\hbar^2 k_0^2}{m}}$$