Lecture 24:

Intro to Quantum Stat Mech, pt 1

Tuckerman Ch 10

Up till now, we've only considered classical statistical mechanics of particles or lattice modes

We were able to understand these systems by considering their energy as a sum of terms that depend on generally pairwise interactions

The particle systems can also have any possible Energy

In QM, all the particles interact, and energy levels tend to be discrete (even if ∞ #)

For the QM operator $\hat{H} = \sum_{i=1}^{N} \hat{p}_i^2/2m + u(r_1, \ldots, r_N)$

x, y, z

we know $[r_{i\alpha}, p_{i\beta}] = i\hbar \delta_{ij} \delta_{\alpha\beta}$

In the coordinate basis, the states are

$\hat{r} = |\vec{r}_1 \vec{r}_2 \ldots \vec{r}_N\rangle = |\vec{r}_1\rangle \otimes |\vec{r}_2\rangle \otimes \ldots \otimes |\vec{r}_N\rangle$

direct product / tensor product

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

in the position basis, call $\vec{x}_i = r_i, s_i$ spin

$$\left[-\frac{\hbar^2}{2m} \sum \nabla_i + U(r_1 \ldots r_N)\right] \Psi(x_1 \ldots x_N, t) = i\hbar \frac{\partial}{\partial t} \Psi(x_1 \ldots x_N, t)$$

observations are $\langle \hat{A} \rangle_t = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle$

To solve this, except for simple cases

have to do it on a grid, M points in each direction

~3N-dim integral means $M^{\sim 3N}$ points

Nor even $N = 10$, dof $= 3N-6$, in gas phase

10^{24} is too big to handle.

for just one time, energy levels

$$H\Psi = E\Psi \quad \ldots \quad \text{have to solve}$$

$$\left[-\hbar/2m \sum_i \nabla_i^2 + U(r_1, \ldots r_N)\right] \Psi_{(k,m)}(x_1, \ldots, x_N)$$

$$= \mathcal{E}_{\{k,m\}} \Psi_{(k,m)}(x_1, \ldots, x_N)$$

where $\vec{K}_1 \ldots \vec{k}_N, m_1 \ldots m_N$ « S_z values are 4N QM #s needed to solve the problem

A few particles is max size for this "exact diagonalization problem"

We want to use statistical methods instead!

Imagine Z - copies of our system, each in state $|\Psi^{(\lambda)}\rangle$, $\lambda = 1 \ldots Z$, imagine fixed in time also

Assume that states come from a distribution corresponding to thermo observable, const E, P, etc

want $\quad \langle \hat{A} \rangle_{ens} = \frac{1}{Z} \sum_{\lambda=1}^{Z} \langle \Psi^{(\lambda)} | \hat{A} | \Psi \rangle$

Can work in a basis $|\Psi^{(\lambda)}\rangle = \sum_k c_k^{(\lambda)} |\phi_k\rangle$

$(c_k^{(\lambda)} = \langle \phi_k | \Psi^{(\lambda)} \rangle)$

Plugging in:

$$\langle \hat{A} \rangle_{ens} = \frac{1}{Z} \sum_\lambda \sum_{k,l} c_k^{(\lambda)*} c_l^{(\lambda)} \langle \phi_k | \hat{A} | \phi_l \rangle$$

$$= \sum_{k,l} \left(\frac{1}{Z} \sum_{\lambda=1}^{Z} c_l^{(\lambda)} c_k^{*(\lambda)} \right) \underbrace{\langle \phi_k | \hat{A} | \phi_l \rangle}_{\equiv A_{kl}}$$

If we define $\rho_{lk} = \sum_\lambda c_l^{(\lambda)} c_k^{(\lambda)*}$ ← matrix entries

& $\tilde{\rho}_{lk} = \rho_{lk}/Z$

$$\langle \hat{A} \rangle_{ens} = \frac{1}{Z} \sum_{kl} \rho_{lk} A_{kl} = \frac{1}{Z} \sum_l (\hat{\rho} \hat{A})_{ll}$$

$$= \frac{1}{Z} \mathrm{Tr}(\hat{\rho} \hat{A}) = \mathrm{Tr}(\tilde{\rho} \hat{A})$$

Ensemble avg = Tr over density matrix

$$\hat{\rho} = \sum_\lambda |\Psi^\lambda\rangle\langle\Psi^\lambda| \quad b/c$$

$$\langle \phi_l | \hat{\rho} | \phi_k \rangle = \sum_\lambda \langle \phi_l | \left(\sum_{a,b} c_a^{(\lambda)} |\phi_a\rangle\langle\phi_b| c_b^{(\lambda)*} \right) | \phi_k \rangle$$

$$= \sum_\lambda c_l^{(\lambda)} c_k^{(\lambda)*} \checkmark$$

This defn shows $\hat{\rho}^\dagger = \hat{\rho}$, $\tilde{\rho}^\dagger = \tilde{\rho}$,

hermitian operator, so

$\tilde{\rho}\,|\omega_k\rangle = \omega_k\,|\omega_k\rangle$, where $|\omega_k\rangle$ are complete orthogonal basis

What do they mean?

$\hat{A} = \hat{I}$

$$\langle \hat{I} \rangle = \mathrm{Tr}(1\,\tilde{\rho}) = \sum \omega_k = 1$$

$\hat{A} = |\omega_m\rangle\langle\omega_m| = \hat{P}_m$ (projection operator)

$$\langle P_m \rangle = \mathrm{Tr}(\tilde{\rho}\,P_m) = \sum_\ell \langle \omega_\ell|\rho|\omega_m\rangle\langle\omega_m|\omega_\ell\rangle$$

$$= \omega_m$$

written another way

$$\langle P_m \rangle = \sum_\ell \langle \omega_\ell|\frac{1}{Z}\sum_{\lambda=1}^{Z}|\psi^{(\lambda)}\rangle\langle\psi^{(\lambda)}|\omega_m\rangle\langle\omega_m|\omega_\ell\rangle$$

$$= \frac{1}{Z}\sum_\lambda |\langle\psi^{(\lambda)}|\omega_m\rangle^2| \geq 0$$

So $\omega_m \geq 0$, & $\sum_m \omega_m = 1 \Rightarrow \omega_m$ also ≤ 1

Can associate ω_m w/ prob of some kind

Turns out (skipping for time) $\{|\omega_m\rangle\}$ are the states & ω_m is the prob of being in that state

So prob of observing $\hat{A}$ is a weighted sum just

if $|a_k\rangle$ are eigenvalues of $\hat{A}$, $P_{a_m} = |a_m\rangle\langle a_m|$

$$\sim \quad \langle P_k \rangle = \sum_m \omega_m |\langle a_k | \omega_m \rangle|^2$$

ρ is like $f(q,p)$ in classical mechanics

Time evolution

$$\rho(t) = \sum_{\lambda=1} |\psi^{(\lambda)}(t)\rangle\langle\psi^{(\lambda)}(t)|$$

$$\frac{\partial \rho(t)}{\partial t} = \sum_\lambda \frac{\partial}{\partial t}|\psi^{(\lambda)}(t)\rangle\langle\psi^{(\lambda)}(t)| + |\psi^{(\lambda)}(t)\rangle \frac{\partial}{\partial t}\langle\psi^{(\lambda)}(t)|$$

but $\frac{\partial}{\partial t}|\psi\rangle = \frac{1}{i\hbar} H|\psi\rangle$

$$\frac{\partial \rho(t)}{\partial t} = \frac{1}{i\hbar}\sum_\lambda \left(H|\psi^{\lambda}(t)\rangle\langle\psi^{\lambda}(t)| - |\psi^{(\lambda)}(t)\rangle\langle\psi^{\lambda}(t)|H\right)$$

$$= 1/i\hbar \left(H\hat{\rho} - \rho\hat{H} \right) = \frac{1}{i\hbar}[H, \hat{\rho}]$$

Quantum Liouville Equation

different by $-$ sign from evolution of observable operator, ρ is not one

Formally $\rho(t) = e^{-iHt/\hbar}\rho(0)e^{+iHt/\hbar} = U(t)\rho(0)U^\dagger(t)$

so if $iL \equiv \frac{1}{i\hbar}[\ldots, H]$, $\frac{\partial \rho}{\partial t} = -i\hat{L}\rho$, $\rho(t) = e^{-i\hat{L}t}\rho(0)$

[$\mathcal{L}$ is a super operator
acts on operator & returns operator]

Quantum Equilibrium Ensembles

Equilibrium means $\frac{\partial \hat{\rho}}{\partial t} = 0$, $[H, \rho] = 0$

like in classical, $F(\hat{A})$ is a solution, so

H & ρ have simultaneous eigenstates

$\hat{\rho}|E_k\rangle = F(H)|E_k\rangle = F(E_k)|E_k\rangle$

Turns out $\rho(\hat{H}) = e^{-\beta H} / Q(N,V,T)$ as in classical

$Q(N,V,T) = \mathrm{Tr}(\rho(\hat{H}))$

In energy eigenbasis $Q(N,V,T) = \sum_k e^{-\beta E_k}$ ← like classical discrete case

$\langle \hat{A} \rangle_{NVT} = \mathrm{Tr}(\tilde{\rho} A) = \frac{1}{Q(N,V,T)} \sum_k e^{-\beta E_k} \langle E_k | A | E_k \rangle$

if E_k's are degenerate

$Q(N,V,T) = \sum_k g(E_k) e^{-\beta E_k}$ and $g(E_k)$ goes in to $\langle A \rangle$

(also true for classical!)

Example: Harmonic Oscillator

$$\mathcal{E}_n = (n + 1/2)\hbar\omega \qquad n = 0, \ldots$$

$$Q(\beta) = \sum_{n=0}^{\infty} e^{-\beta \mathcal{E}_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \overset{\text{zero pt}}{e^{-\beta\hbar\omega/2}} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n$$

$$\sum r^n = 1/(1-r) \quad \text{if} \quad 0 < r < 1$$

$$= e^{-\beta\hbar\omega/2} \cdot \frac{1}{1-e^{-\beta\hbar\omega}} = \left(e^{+\beta\hbar\omega/2} + e^{-\beta\hbar\omega/2}\right)^{-1}$$

Just like classical, if N independent oscillators $Q_N = Q^N \ (1/N!)$

$$A = -\frac{1}{\beta}\ln Q = \frac{\hbar\omega}{2} + \frac{1}{\beta}\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$\mathcal{E} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial\beta}\left[-\frac{\beta\hbar\omega}{2} - \log\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

$$= \underbrace{\hbar\omega/2}_{\text{zero pt}} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \hbar\omega\left(\langle n \rangle + \frac{1}{2}\right)$$

Hard part is still how to solve eigenvalue problem for H, but we can continue seeing other consequences

Tuckerman Ch 11, Fermi-Dirac / Bose-Einstein Stats

Symmetry conditions on the wave function make ideal gas of fermions / bosons more interesting than classical particles

$\mathcal{H} = \sum p_i^2/2m$, completely separable

$\hat{\mathcal{H}} = \sum_i \hat{h}_i$, and so solutions to total schrodinger equation are products of single particle wave functions

$h_i \psi = e_i \psi$, $\quad E_{total} = \sum_{i=1}^{N} e_i$,

Solution wave funcs also have separable spin part

eigenvalues - $\chi_m(s) = \langle s | \chi_m \rangle = \delta_{ms}$,

$\chi_\uparrow(\uparrow) = 1$, $\quad \chi_\downarrow(\uparrow) = 0$ etc

We know solutions to this one particle problem

$$\psi_n(x_i, y_i, z_i) = \left(\frac{1}{L}\right)^{3/2} \exp\left(\frac{2\pi i}{L}(n_i^x x_i + n_i^y y_i + n_i^z z_i)\right) = \frac{1}{\sqrt{V}} e^{2\pi i (n_i \cdot r_i)}$$

w/ $p_n = \frac{2\pi\hbar}{L} n_i$ & $\varepsilon_n = \frac{2\pi^2\hbar^2}{mL^2} |n_i|^2 = p^2/2m$

Complete wave func $\phi_{\vec{n}_i, m_i}(\vec{r}_i) = \frac{1}{\sqrt{V}} e^{2\pi i \, \vec{n}_i \cdot \vec{r}_i / L} \chi_{m_i}(s_i)$

In order to make a fully symmetrized wave func for the total system, s.t. for fermions exchange of particles changes the sign & not bosons, construct

$$M = \begin{pmatrix} \phi_{n_1,m_1}(x_1) & \phi_{n_2,m_2}(x_1) & \cdots & \phi_{n_N m_N}(x_1) \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_{n_1,m_1}(x_N) & \cdots & \cdots & \phi_{n_N m_N}(x_N) \end{pmatrix}$$

$\psi(x_1 \dots x_N) = \det M$ (Slater det)

$\psi(x_1 \dots x_N) = \text{perm } M \leftarrow$ det w/ all $-$'s changed to $+$

Now the stat mech part. How many particles have a particular $\vec{n}$ & spin $S_z = m$

call $f_{\vec{n}m}$ this occupation number

Know $\sum_m \sum_{\vec{n}} f_{\vec{n}m} = N$ $\left(\sum_{\vec{n}} = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} \right)$

$\left(\sum_m = \sum_{m=-s}^{s} \right.$

Then $E_{\{f_{nm}\}} = \sum_m \sum_{\vec{n}} \epsilon_{\vec{n}} f_{\vec{n}m}$ (second quantization)