Quantum Mechanical aspects of Stat. Mech.

In the canonical ensemble: $Q = \sum_{j} e^{-\beta E_j}$ ← energies of states

↑ states

$$\langle M \rangle = \frac{1}{Q} \sum_j M_j e^{-\beta E_j}$$

↑ property or observable M in state j

Quantum Mechanically, if we have a set of <u>energy eigenstates</u> $|\psi_j\rangle$ much of this works the same:

$$\hat{\mathcal{H}} |\psi_j\rangle = E_j |\psi_j\rangle$$

Hamiltonian operator

↑ wavefunction (energy eigenfunction)

An aside:

$$\hat{\mathcal{H}}^2 |\psi_j\rangle = \hat{\mathcal{H}}\hat{\mathcal{H}} |\psi_j\rangle = \hat{\mathcal{H}} E_j |\psi_j\rangle = E_j \hat{\mathcal{H}} |\psi_j\rangle = E_j^2 |\psi_j\rangle$$

In general:

$$\hat{\mathcal{H}}^n |\psi_j\rangle = E_j^n |\psi_j\rangle \quad \text{for integer } n$$

This implies:

$$e^{-\beta\hat{\mathcal{H}}} |\psi_j\rangle = \left(\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \hat{\mathcal{H}}^n\right) |\psi_j\rangle = \left(\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} E_j^n\right) |\psi_j\rangle$$

$$= e^{-\beta E_j} |\psi_j\rangle$$

If we left-multiply by the complex conjugate $\langle\psi_j|$:

$$\langle\psi_j| \underbrace{e^{-\beta E_j}}_{\text{Just a scalar}} |\psi_j\rangle = \langle\psi_j| e^{-\beta\hat{\mathcal{H}}} |\psi_j\rangle$$

$$= \int \psi_j^*(\vec{r})\, e^{-\beta\hat{\mathcal{H}}}\, \psi_j(\vec{r})\, d\vec{r}$$

$$e^{-\beta E_j} \underbrace{\langle\psi_j|\psi_j\rangle}_{= 1 \text{ for orthonormal set}} = \langle\psi_j| e^{-\beta\hat{\mathcal{H}}} |\psi_j\rangle$$

$$e^{-\beta E_j} = \langle\psi_j| e^{-\beta\hat{\mathcal{H}}} |\psi_j\rangle$$

So we may write $Q = \sum_j e^{-\beta E_j} = \sum_j \langle \psi_j | e^{-\beta \hat{\mathcal{H}}} | \psi_j \rangle$

We can also define other matrix elements

$$\langle \psi_i | e^{-\beta \hat{\mathcal{H}}} | \psi_j \rangle = \int \psi_i^*(\vec{r})\, e^{-\beta \hat{\mathcal{H}}}\, \psi_j(\vec{r})\, d\vec{r}$$

$$= \left[e^{-\beta \hat{\mathcal{H}}} \right]_{ij}$$

$$\therefore \quad Q = \sum_j \left[e^{-\beta \hat{\mathcal{H}}} \right]_{jj} \equiv Tr\left[e^{-\beta \hat{\mathcal{H}}} \right]$$

This is the QM statement of canonical PF!

The trace is independent of basis set, so if we have another set of orthonormal functions (i.e. not energy eigenstates):

$$\underset{\text{a new set of functions}}{|\phi_j\rangle} = \sum_n \underbrace{a_{jn} |\psi_n\rangle}_{\text{expanded in energy eigenstates}}$$

What are the a_{jn} values?

$$\langle \psi_k | \phi_j \rangle = \sum_n a_{jn} \langle \psi_k | \psi_n \rangle$$

$$= \sum_n a_{jn} \delta_{kn}$$

$$\langle \psi_k | \phi_j \rangle = a_{jk} \quad \Rightarrow \quad a_{jn} = \langle \psi_n | \phi_j \rangle$$

If $|\phi_j\rangle$ are orthonormal, it is easy to prove:

$$1 = \sum_n a_{jn}^* a_{jn} = \underbrace{\sum_n \langle \phi_j | \psi_n \rangle \langle \psi_n}_{\text{Complete basis expansion} = 1} | \phi_j \rangle$$

$$\sum_n a_{jn}^* a_{jn} = \langle \phi_j | \phi_j \rangle = \int \phi_j^*(\vec{r})\, \phi_j(\vec{r})\, d\vec{r} = 1$$

We also need the reverse expansion:

$$|\psi_s\rangle = \sum_t b_{st} |\phi_t\rangle \quad \text{with} \quad b_{st} = \langle \phi_t | \psi_s \rangle$$

$$b_{st} = \langle \phi_t | \psi_s \rangle = a_{ts}^*$$

$$\therefore \quad \sum_n b_{jn}^* b_{jn} = \sum_n a_{nj} a_{nj}^* = 1$$

This is all going somewhere!

$$Q = \sum_j \langle \psi_j | e^{-\beta \hat{H}} | \psi_j \rangle = \sum_j \langle \phi_j | e^{-\beta \hat{H}} | \phi_j \rangle$$

Now, on to observables:

$$\langle M \rangle = \frac{\sum_j M_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \qquad M_j = \int \psi_j^*(\vec{r}) \hat{M} \psi_j(\vec{r}) d\vec{r} = \langle \psi_j | \hat{M} | \psi_j \rangle$$

$$\therefore \quad \sum_j M_j e^{-\beta E_j} = \sum_j e^{-\beta E_j} \langle \psi_j | \hat{M} | \psi_j \rangle$$

$$= \sum_j \langle \psi_j | \hat{M} e^{-\beta E_j} | \psi_j \rangle$$

$$= \sum_j \langle \psi_j | \hat{M} e^{-\beta \hat{H}} | \psi_j \rangle$$

$$= Tr\left[\hat{M} e^{-\beta \hat{H}} \right]$$

$$\therefore \quad \langle M \rangle = \frac{Tr\left[\hat{M} e^{-\beta \hat{H}} \right]}{Tr\left[e^{-\beta \hat{H}} \right]} \longleftarrow \text{a scalar}$$

So, we define an operator:

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Tr\left[e^{-\beta \hat{H}} \right]} = \text{density operator or density matrix}$$

$\hat{\rho}$ has off-diagonal elements:

$$\langle i|\hat{\rho}|j\rangle = \frac{\int \psi_i^*(\vec{r})\, e^{-\beta\hat{\mathcal{H}}}\, \psi_j(\vec{r})\, d\vec{r}}{\sum_j \int \psi_j^*(\vec{r})\, e^{-\beta\hat{\mathcal{H}}}\, \psi_j(\vec{r})\, d\vec{r}} = [\hat{\rho}]_{ij}$$

$$\langle M\rangle = Tr[\hat{M}\hat{\rho}]$$

Time-dependence:

$$-i\hbar \frac{\partial}{\partial t} |\phi_j\rangle = \hat{\mathcal{H}} |\phi_j\rangle$$

$$\therefore \quad |\phi_j(t)\rangle = \underbrace{e^{-i\hat{\mathcal{H}}t/\hbar}}_{\text{propagator}} |\phi_j(0)\rangle$$

The overlap of a state with itself at a later time:

$$\langle\phi_j(0)|\phi_j(t)\rangle = \langle\phi_j(0)|\, e^{-i\hat{\mathcal{H}}t/\hbar}\, |\phi_j(0)\rangle$$

In Q we have:

$$\sum_j \langle\phi_j|\, e^{-\beta\hat{\mathcal{H}}}\, |\phi_j\rangle$$

these look quite similar, right?

$e^{-i\hat{\mathcal{H}}t/\hbar}$ is a propagator in <u>real</u> time.

Consider an <u>imaginary</u> time $-i\beta\hbar$ $\therefore$ $e^{-i\hat{\mathcal{H}}t/\hbar} = e^{-i\hat{\mathcal{H}}(-i\beta\hbar)/\hbar} = e^{-\beta\hat{\mathcal{H}}}$

$\therefore$ The Boltzmann operator is like a propagator in imaginary time $-i\beta\hbar = \dfrac{-i\hbar}{k_B T}$ $\leftarrow \dfrac{\text{energy}\cdot\text{time}}{\text{energy}}$

Q is tied to the overlaps of states in imaginary time

$$Q = \sum_j \langle\phi_j(0)|\phi_j(-i\beta\hbar)\rangle$$

Evolution of a state is usually handled by breaking up time into small discrete pieces:

$$e^{-i\hat{\mathcal{H}}t/\hbar} \rightarrow \left(e^{-i\mathcal{H}\delta t/\hbar}\right)^P \leftarrow \text{lots of pieces}$$

$$\delta t = \frac{t}{P}$$

The δt bits are timesteps for a trajectory or path integral. Likewise:

$$e^{-\beta\hat{\mathcal{H}}} \longrightarrow \left(e^{-(\beta/P)\hat{\mathcal{H}}}\right)^P$$

small bits of imaginary time

So:

$$Q = \int d\vec{r}^{(1)} \int d\vec{r}^{(2)} \cdots \int d\vec{r}^{(P)} \langle \vec{r}^{(1)} | e^{-\varepsilon\hat{\mathcal{H}}} | \vec{r}^{(2)} \rangle \times \langle \vec{r}^{(2)} | e^{-\varepsilon\hat{\mathcal{H}}} | \vec{r}^{(3)} \rangle \cdots \langle \vec{r}^{(P)} | e^{-\varepsilon\hat{\mathcal{H}}} | \vec{r}^{(1)} \rangle$$

with $\epsilon = \frac{\beta}{P}$ (If we assume $P \to \infty$, $\epsilon \to 0$)

Also suppose we separate $\hat{\mathcal{H}}$ into a reference $\hat{\mathcal{H}}_0$ and a remainder:

$$e^{-\epsilon\hat{\mathcal{H}}} = e^{-\epsilon(\hat{\mathcal{H}}_0 + \hat{V})} = \underbrace{e^{-\epsilon\mathcal{H}_0} e^{-\epsilon V} \times (1 + O(\epsilon^2))}_{V \,\&\, \mathcal{H}_0 \text{ don't necessarily commute}}$$

For large P, we have

$$\langle \vec{r} | e^{-\epsilon\hat{\mathcal{H}}} | \vec{r}' \rangle \sim \rho_0(\vec{r}, \vec{r}'; \epsilon)\, e^{-\epsilon V(\vec{r})}$$

$$\text{where} \quad \rho_0(\vec{r}, \vec{r}'; \epsilon) = \langle \vec{r} | e^{-\epsilon\hat{\mathcal{H}}_0} | \vec{r}' \rangle$$

Isomorphism

$$Q = Tr[e^{-\beta \hat{\mathcal{H}}}]$$

$\Leftarrow$ independent of basis set

for a continuous basis, $\langle \vec{r}|$, $|\vec{r}\rangle$ $\leftarrow$ generalized 3N vector of positions

$$Q = \int d\vec{r} \langle \vec{r} | e^{-\beta \hat{\mathcal{H}}} | \vec{r} \rangle$$

propagator

$$e^{-i\hat{\mathcal{H}}t/\hbar} |\vec{r}(0)\rangle = |\vec{r}(t)\rangle$$

$$e^{-\beta\hat{\mathcal{H}}} |\vec{r}(0)\rangle = |\vec{r}(-i\beta\hbar)\rangle$$

Boltzmann operator is like a propagator in imaginary time!

Evolution is done by breaking propagator up into smaller timesteps:

$$e^{-i\hat{\mathcal{H}}t/\hbar} \approx \underbrace{\left(e^{-i\hat{\mathcal{H}}\delta t/\hbar}\right)}_{\text{propagates for } \delta t}{}^{P} \qquad t = p\delta t$$

We usually do this with a linearized or approximate Hamiltonian in classical mechanics.

We can do the same in imaginary time:

$$e^{-\beta\hat{\mathcal{H}}} \approx \left(e^{-(\beta/p)\hat{\mathcal{H}}}\right)^{P} \quad \leftarrow \text{each timestep is separated}$$

An expansion in a complete set of states:

$$\sum_j |j\rangle\langle j|$$

In a continuous basis:

$$\int d\vec{r}^{(1)} |\vec{r}^{(1)}\rangle\langle \vec{r}^{(1)}|$$

$\therefore$

$$Q = \int d\vec{r}^{(1)} \int d\vec{r}^{(2)} \dots \int d\vec{r}^{(P)} \langle \vec{r}^{(1)} | e^{-\epsilon\mathcal{H}} | \vec{r}^{(2)} \rangle \langle \vec{r}^{(2)} | e^{-\epsilon\mathcal{H}} | \vec{r}^{(3)} \rangle \dots \langle \vec{r}^{(P)} | e^{-\epsilon\mathcal{H}} | \vec{r}^{(1)} \rangle$$

with $\epsilon = \beta P$

Another trick:

$$e^{-\epsilon \mathcal{H}} = e^{-\epsilon(\mathcal{H}_0 + V)} \approx e^{-\epsilon \mathcal{H}_0} e^{-\epsilon V} \left[1 + O(\epsilon^2) \right]$$

$\Leftarrow$ $\hat{\mathcal{H}}_0$ & $\hat{V}$ don't commute

For large enough p (small enough ϵ):

$$\langle \vec{r} | e^{-\epsilon \hat{\mathcal{H}}} | \vec{r}\,' \rangle \approx \rho_0(\vec{r}, \vec{r}\,'; \epsilon)\, e^{-\epsilon V(\vec{r})}$$

where

$\rho_0(\vec{r}, \vec{r}\,'; \epsilon)$ = unperturbed density matrix for $\underline{\hat{\mathcal{H}}_0}$

$\therefore$

$$Q = \lim_{p \to \infty} \int d\vec{r}^{(1)} \cdots \int d\vec{r}^{(p)} \left[\prod_{\alpha=1}^{p} \rho_0(\vec{r}^{(\alpha)}, \vec{r}^{(\alpha+1)}; \epsilon)\, e^{-\epsilon V(\vec{r}^{(\alpha)})} \right]$$

with a periodic condition $\vec{r}_p = \vec{r}_1$

p-fold integrals are <u>path</u> or <u>functional</u> integrals!

Q_p = Q with p discrete points

=

o~o $= \rho_0(r^{(\alpha)}, r^{(\alpha+1)}, \epsilon)$

o— $= e^{-\epsilon V(r^{\alpha})}$

= ring polymer with nearest neighbor interactions!

Why would we split up $\hat{\mathcal{H}}_0$ & $\hat{V}$?

$\hat{\mathcal{H}}_0$ might be for N free particles (e.g. only kinetic energy)

If $\hat{\mathcal{H}}_0 = \frac{\hat{p}^2}{2m}$, Then

$$\rho_0(\vec{r},\vec{r}\,';\epsilon) = \langle \vec{r}\,|\, e^{-\epsilon \hat{p}^2/2m} \,|\vec{r}\,'\rangle$$

The eigenstates of $\hat{p}\,|\vec{k}\rangle = \hbar \vec{k}\,|\vec{k}\rangle$

$$\hat{p} \to -i\hbar \frac{\partial}{\partial \vec{r}} \qquad |\vec{k}\rangle \to \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\text{free particle wavefunction}}$$

So:

$$\rho_0(\vec{r},\vec{r}\,';\epsilon) = \frac{1}{(2\pi)^3}\int d\vec{k}\, \langle \vec{r}\,|\vec{k}\rangle\, e^{-\epsilon\hbar^2 k^2/2m} \langle \vec{k}\,|\vec{r}\,'\rangle$$

$$= \frac{1}{(2\pi)^3}\int d\vec{k}\; e^{-i\vec{k}(\vec{r}-\vec{r}\,')}\, e^{-\epsilon\hbar^2 k^2/2m}$$

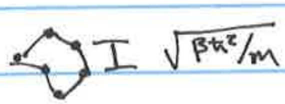
$$= \left(\frac{m}{2\pi\hbar^2\epsilon}\right)^{3/2} e^{-m|\vec{r}-\vec{r}\,'|^2/2\hbar^2\epsilon}$$

= Gaussian with variance $\frac{\epsilon\hbar^2}{m}$

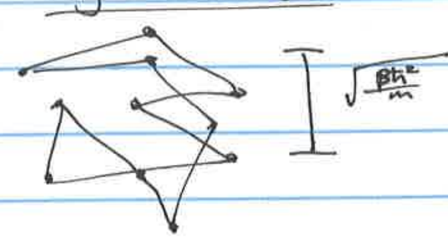
$$Q_P = \int \left[\prod_{i=1}^{N}\prod_{\alpha=1}^{P} d\vec{r}_i^{\,(\alpha)}\right] \left\{ \prod_{i=1}^{N}\prod_{\alpha=1}^{P} \left(\frac{m}{2\pi\hbar^2\epsilon}\right)^{3/2} e^{-m|\vec{r}_i^{\,\alpha}-\vec{r}_i^{\,\alpha+1}|^2/2\hbar^2\epsilon}\, e^{-V(r_i^{\alpha})} \right\}$$

The variance to a nearest-neighbor bead is like a spring's variance $\left(\frac{\epsilon\hbar^2}{m}\right)$. Variance of an unperturbed circular path is $\frac{\beta\hbar^2}{m}$

Heavy Particles



Light Particles



$$\lambda = \left(\frac{\beta\hbar^2}{m}\right)^{1/2}$$ = uncertainty or thermal wavelength of particle of mass m