Statistical Ensembles in QM

* So far, we've treated the stat. mech. of QM systems in a not-very-rigorous way.

* I.e., we've made allowances for the fact that microstates can be discrete (i.e., $Z = \sum_i e^{-\beta E_i}$) due to energy being quantized, etc. But we've run into difficulties dealing w/ the fact that in QM, we have to count the distinct microstates carefully due to the indistinguishability of identical particles.

* This led to inconsistencies in our treatment of the ideal gas (non-extensive entropy, etc.) that were corrected (approximately ... only valid for dilute systems @ high T so $\langle n_k \rangle \ll 1$) in an ad-hoc way (i.e. $Z_N = (Z_1)^N \rightarrow \frac{1}{N!}(Z_1)^N$)

* To do things 100% consistently, we need to better understand ensemble theory in the language of Hilbert space (i.e., state vectors + operators)

* Once we do this, there's no need for ad-hoc $\frac{1}{N!}$ correction factors, + things will work correctly at all densities + temperatures

* This in turn will open up exciting new purely QM phenomena (Bose-Einstein condensation, superfluids, etc...)

Concept	CM	QM
① microstate at time t	$(\vec{q}_1(t) \dots \vec{q}_N(t), \dots \vec{p}_N(t))$	$\vert\Psi(t)\rangle$
② time evolution of microstate	$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial \dot{p}_i}$ $\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial \dot{q}_i}$	$i\hbar \frac{\partial}{\partial t}\vert\Psi(t)\rangle = \hat{H}\vert\Psi(t)\rangle$ $\Downarrow$ $\vert\Psi(t)\rangle = e^{-i\frac{\hat{H}(t-t_0)}{\hbar}}\vert\Psi(t_0)\rangle$
③ Some physical observable in a μ-state	$\mathcal{O}(q_i, p_i)$ uniquely determined in a fixed microstate	$\langle\Psi(t)\vert\hat{\mathcal{O}}\vert\Psi(t)\rangle$ NOT uniquely determined in a fixed microstate (random variable - only average value is predicted)
④ Ensemble Average	$\overline{\mathcal{O}}(t) = \frac{\int d\Gamma\, \mathcal{O}(p,q)\, \rho(p,q;t)}{\int d\Gamma\, \rho(p,q,t)}$	?

* To figure out what the appropriate QM version of an ensemble average is, let's 1st re-write the classical version slightly

$$\overline{O} = \frac{\int d\Gamma \, O(p,q)\, \rho(p,q;t)}{\int d\Gamma \, \rho(p,q;t)} \equiv \int d\Gamma \, O(p,q)\, \tilde{\rho}(p,q,t)$$

where $\tilde{\rho}(p,q;t) = \dfrac{\rho(p,q;t)}{\int d\Gamma \, \rho(p,q;t)}$

$$\therefore \; \tilde{\rho}(p,q;t)\, d\Gamma = \frac{dN(p,q;t)}{N}$$

# of ensemble points in $d\Gamma$ about (p,q)

total # of ensemble systems

$\Rightarrow$ $\tilde{\rho}$ is a probability density, can formally re-write as

$$\tilde{\rho}(p,q;t) = \sum_{\alpha=1}^{N} P_\alpha \prod_{i=1}^{N} \delta^3(\vec{q}_i - \vec{q}_{i,\alpha}(t))\, \delta^3(\vec{p}_i - \vec{p}_{i,\alpha}(t))$$

P_α = probability of the α^{th} ensemble system

$$\Rightarrow \boxed{\overline{O}(t) = \sum_{\alpha=1}^{N} P_\alpha \, O_\alpha(t)}$$

where $O_\alpha(t) \equiv O(\vec{p}_{1,\alpha}(t)\, \vec{p}_{2,\alpha}(t) \cdots \vec{p}_{N,\alpha}(t), \vec{q}_{1,\alpha}(t) \cdots \vec{q}_{N,\alpha}(t))$

i.e., value of O for the α^{th} ensemble point at time t.

* In this form, we see a reasonable QM generalization is

$$\boxed{\overline{O}(t) = \sum_{\alpha=1}^{N} p_\alpha \langle \Psi^{(\alpha)}(t) | \hat{O} | \Psi^{(\alpha)}(t) \rangle}$$

where $\sum_{\alpha=1}^{N} p_\alpha = 1$

<u>Note</u>: There is no assumption that $\{|\Psi^{(\alpha)}\rangle\}$ is a complete orthonormal set. They are simply different microstates that are consistent w/ the given macrostate.

* Let $\sum_n |n\rangle\langle n| = \mathbb{1}$ be some orthonormal complete basis

$$|\Psi^{(\alpha)}(t)\rangle = \sum_n |n\rangle\langle n|\Psi^{(\alpha)}(t)\rangle = \sum_n |n\rangle C_{n\alpha}(t)$$

$$\Rightarrow \overline{O}(t) = \sum_{n,m} \underbrace{\left(\sum_\alpha C_{n\alpha}(t) C^*_{m\alpha}(t) p_\alpha\right)}_{\substack{\parallel \\ \rho_{nm}(t)}} \langle m|O|n\rangle$$

$\rho_{nm}(t)$ "<u>density matrix</u>"

$$\Rightarrow \boxed{\begin{aligned} &\overline{\mathcal{O}}(t) = \sum_{n,m} \rho_{nm}(t)\, \mathcal{O}_{mn} = \mathrm{Tr}(\hat{\rho}\hat{\mathcal{O}}) \\ &\hat{\rho} = \sum_{\alpha} p_\alpha |\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)| \quad \text{"density operator"} \end{aligned}}$$

Some properties of $\hat{\rho}$

① **Normalization**

$$\begin{aligned} \mathrm{Tr}\,\hat{\rho} &= \mathrm{Tr}\Big(\sum_\alpha p_\alpha |\Psi^{(\alpha)}\rangle\langle\Psi^{(\alpha)}|\Big) \\ &= \sum_n \sum_\alpha p_\alpha \langle n|\Psi^{(\alpha)}\rangle\langle\Psi^{(\alpha)}|n\rangle \\ &= \sum_\alpha p_\alpha \sum_n \langle\Psi^{(\alpha)}|n\rangle\langle n|\Psi^{(\alpha)}\rangle \\ &= \sum_\alpha p_\alpha \overbrace{\langle\Psi^{(\alpha)}|\Psi^{(\alpha)}\rangle}^{1} \end{aligned}$$

$$\Rightarrow \boxed{\mathrm{Tr}\,\hat{\rho} = 1}$$

② **Hermitian** $\hat{\rho} = \hat{\rho}^\dagger$

$$\Downarrow \text{ diagonalizable}$$

$$\hat{\rho}|\rho_i\rangle = w_i|\rho_i\rangle \Rightarrow \boxed{\begin{aligned} &\hat{\rho} = \sum_i w_i |\rho_i\rangle\langle\rho_i| \\ &\text{where } \sum_i |\rho_i\rangle\langle\rho_i| = 1 \end{aligned}}$$

③ **Pos. definite**: $\langle\Phi|\hat{\rho}|\Phi\rangle = \sum_\alpha p_\alpha |\langle\Phi|\Psi^{(\alpha)}\rangle|^2 \geq 0$

(for any $|\Phi\rangle$)

$\therefore$ Taking $|\Phi\rangle = |\rho_i\rangle$,

$$\langle \rho_i|\rho|\rho_i\rangle = w_i = \sum_\alpha P_\alpha |\langle \rho_i|\Psi^{(\alpha)}\rangle|^2 \geq 0$$

$$\boxed{\therefore \text{ all } w_i \geq 0}$$

Since $\mathrm{Tr}\,\hat{\rho} = 1$, then ① $\sum_i w_i = 1$
② $0 \leq w_i \leq 1$ } can interpret w_i as probabilities

④ <u>Pure states</u>: $\hat{\rho}^2 = \hat{\rho}$ iff $\hat{\rho} = |\Psi\rangle\langle\Psi|$

Since $|\Psi\rangle \cancel{\langle\Psi|\Psi\rangle}^{1} \langle\Psi| = |\Psi\rangle\langle\Psi|$

<u>Time Evolution + QM version of Liouville's theorem</u>

* Ultimately we want to describe equilibrium systems
* In classical SM, we showed

$$\frac{d}{dt}\rho(p,q;t) = \frac{\partial}{\partial t}\rho(p,q;t) + \{\rho, \mathcal{H}\}_{PB} = 0$$

$\therefore$ If we wanted equilibrium ρ (i.e., $\frac{\partial}{\partial t}\rho = 0$), then we ~~to~~ needed $\rho = \rho(\mathcal{H}(p,q))$.

The QM version is very similar, since you might recall Dirac's observation that

$$\{A, B\}_{PB} \xrightarrow{QM} \frac{1}{i\hbar}[\hat{A}, \hat{B}]$$

$$\hat{\rho} = \sum_{\alpha} P_\alpha |\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)|$$

$$\therefore i\hbar \frac{\partial \hat{\rho}}{\partial t} = \sum_{\alpha} P_\alpha \Big(i\hbar \frac{\partial}{\partial t}|\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)|$$

$$+ i\hbar |\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)| \overleftarrow{\frac{\partial}{\partial t}} \Big)$$

Use $\quad i\hbar \frac{\partial}{\partial t}|\Psi^{(\alpha)}(t)\rangle = \hat{H}|\Psi^{(\alpha)}(t)\rangle$

$$-i\hbar \frac{\partial}{\partial t}\langle\Psi^{(\alpha)}(t)| = \langle\Psi^{(\alpha)}(t)|\hat{H}$$

$$\boxed{\therefore i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)]}$$

$\therefore$ Want $\hat{\rho} = \hat{\rho}[\hat{H}]$ to get $[\hat{H}, \hat{\rho}] = 0$

$\therefore$ Can simultaneously diagonalize $\hat{\rho}$ & $\hat{H}$

$$\Rightarrow \boxed{\hat{\rho} = \sum_i w_i |E_i\rangle\langle E_i|} \quad \textcircled{x}$$

justifies our earlier ad-hoc treatment of writing the partition function etc in terms of fixed energy states

Eq. ⓧ is really the main result. Now it's just a matter of applying the same logic we used before to derive w_i for MCE, CE & GCE.

* MCE:

$$\hat{\rho}_{MCE}(E) = \sum_i \frac{\delta_{E,E_i}}{\Omega(E)} |E_i\rangle\langle E_i| \Rightarrow w_i = \frac{1}{\Omega(E)}$$

* CE:

$$w_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

$$\Rightarrow \boxed{\hat{\rho}_{CE} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}}$$

entropy $S = -k_B \sum_n w_n \log w_n$

$$= -k_B \sum_n \langle E_n | \hat{\rho} \log \hat{\rho} | E_n \rangle$$

$$\boxed{S = -k_B \operatorname{Tr} \hat{\rho} \log \hat{\rho}}$$

GCE:

$$\boxed{\begin{gathered} w_{n,N} = \frac{e^{-\beta(E_n^N - \mu N)}}{Z_{GCE}} \\ Z_{GCE} = \sum_N \sum_n e^{-\beta(E_n^N - \mu N)} \end{gathered}}$$

$$= \operatorname{Tr}_{FS} e^{-\beta(\hat{H} - \mu \hat{N})}$$

where

is a trace over the Fock Space

(drop the subscript hereafter unless it's ambiguous)

i.e., $\operatorname{Tr}_{FS} \hat{O} = \sum_N \sum_n \langle E_n^N | \hat{O} | E_n^N \rangle$

$$\boxed{\therefore \hat{\rho}_{GCE} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\operatorname{Tr} e^{-\beta(\hat{H} - \mu \hat{N})}}}$$

* While the above development might seem like a very small progress from our earlier ad-hoc treatment of QM systems, the real payoff will come when dealing with identical particles, as it will get rid of the need for ad-hoc correction factors (Gibbs etc.)

* By expressing ensemble averages as

$$\overline{O} = \mathrm{Tr}\,\hat{\rho}\hat{O} = \sum_n \langle E_n|\hat{\rho}\hat{O}|E_n\rangle$$

$$= \sum_n w_n \langle E_n|\hat{O}|E_n\rangle$$

we know how to correctly treat N identical particles in the wf's $|E_n\rangle$, which will lead us to the correct treatment of N identical particles (Bosons or Fermions) example: Find $\hat{\rho}_{CE}$ for a free particle in a box (periodic b.c.'s), and find $\langle \hat{H} \rangle$.

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

$$\psi_E(\vec{x}) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{x}} \quad ; \quad E = \frac{\hbar^2 \vec{k}^2}{2m}$$

$$\psi_E(x+L,y,z) = \psi_E(x,y+L,z) = \psi(x,y,z+L) = \psi_E(x,y,z)$$

$$\Rightarrow \vec{k}_{n_x n_y n_z} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad n = 0, \pm 1, \pm 2, \ldots$$

* Can use any basis to evaluate $\hat{\rho}_{CE}$ in

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \sum_{n_x n_y n_z} \langle \vec{x} | E_{\vec{n}} \rangle \langle E_{\vec{n}} | \vec{x}' \rangle e^{-\beta \frac{\hbar^2 k_n^2}{2m}}$$

$$= \sum_{n_x n_y n_z} \frac{1}{L^3} e^{i \vec{k}_{\vec{n}} \cdot (\vec{x}-\vec{x}')} e^{-\frac{\beta \hbar^2 k_n^2}{2m}}$$

* Use $\frac{1}{L}\sum_{n_x} \xrightarrow{L \gg 1} \int \frac{dk_x}{2\pi}$

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} e^{-\beta \frac{\hbar^2 \vec{k}^2}{2m}}$$

$$\Rightarrow \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x}' \rangle = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{x}-\vec{x}')} e^{-\beta\frac{\hbar^2 \vec{k}^2}{2m}}$$

For each cartesian component, have

$$\int \frac{dk_i}{(2\pi)} e^{i k_i \Delta x_i - \frac{\beta\hbar^2}{2m} k_i^2}$$

$$= \int \frac{dk_i}{(2\pi)} e^{-\frac{\beta\hbar^2}{2m}\left(k_i^2 - \frac{2m}{\beta\hbar^2} i k_i \Delta x_i\right)}$$

$$k_i^2 - \frac{i2mk_i}{\beta\hbar^2}\Delta x_i = \left[\left(k_i - \frac{im\Delta x_i}{\beta\hbar^2}\right)^2 + \frac{m^2\Delta x_i^2}{\beta^2\hbar^4}\right]$$

$$= e^{-\frac{m\Delta x_i^2}{2\beta\hbar^2}} \underbrace{\int \frac{dk_i}{(2\pi)} e^{-\frac{\beta\hbar^2}{2m}\left(k_i - \frac{im\Delta x}{\beta\hbar^2}\right)^2}}_{= \frac{1}{(2\pi)} \times \sqrt{\frac{\pi}{\alpha}}} \qquad \alpha = \frac{\beta\hbar^2}{2m}$$

$$\Rightarrow \boxed{\langle \vec{x} | e^{-\beta\hat{H}} | \vec{x}' \rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}|\vec{x}-\vec{x}'|^2}}$$

* lastly, $\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$, so

$$Z = \mathrm{Tr}\, e^{-\beta \hat{H}} = \int_{L^3} d\vec{x}\, \langle \vec{x} | e^{-\beta \hat{H}} | \vec{x} \rangle$$

$$= L^3 \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}$$

$$\boxed{\langle \vec{x} | \hat{\rho}_{CE} | \vec{x}' \rangle = \frac{1}{V} e^{-\frac{m}{2\beta \hbar^2} |\vec{x} - \vec{x}'|^2}}$$

* To get $\langle \hat{H} \rangle$, need to evaluate

$$\langle \hat{H} \rangle = \mathrm{Tr}\, \hat{H} \hat{\rho}_{CE}$$

This time, let's use $\{ |E_{\vec{n}}\rangle \}$ states to do the trace.

$$\langle \hat{H} \rangle = \frac{1}{Z} \sum_{n_x n_y n_z} \langle E_{\vec{n}} | \hat{H} e^{-\beta \hat{H}} | E_{\vec{n}} \rangle$$

$$= \frac{1}{Z} \sum_{n_x n_y n_z} e^{-\beta \frac{\hbar^2 \vec{k}_n^2}{2m}} \frac{\hbar^2 \vec{k}_n^2}{2m}$$

$$= \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \sum_{\vec{n}} e^{-\beta \frac{\hbar^2 \vec{k}_n^2}{2m}} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z$$

* but $Z = V \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$

$$\therefore \frac{\partial Z}{\partial \beta} = -\frac{3}{2}\left(\frac{Vm}{2\pi\beta\hbar^2}\right)^{3/2} \cdot \frac{1}{\beta} = -\frac{3}{2} Z \frac{1}{\beta}$$

$$\boxed{\therefore \langle \hat{H} \rangle = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2} k_B T \quad \checkmark}$$