Density of states

$$\omega(E) = \frac{1}{N!}\int \frac{dq_i \int dp_i}{h^{3N}} e^{-\beta H(q_i p_i)} \delta(H(q_i, p_i) - E)$$

$\omega(E)$ has units 1/energy because of the δ-function

~~[illegible]~~ To get a pure number, in order to define the entropy, we need to multiply by a const with units of energy

$$\Omega(E) = \omega(E)\Delta$$

or equivalently $\Omega(E) = \int_E^{E+\Delta} dE'\, \omega(E')$ # states in energy shell of thickness Δ

Classically Δ is an arbitrary const in the above, similar to h. When we go to QM, h becomes Planck's const and Δ becomes of order the energy spacing

Canonical ensemble

$$Q_N(T) = \int dE\, \omega(E) e^{-\beta E}$$

$$= \int \frac{dE}{\Delta}\, \omega(E)\Delta e^{-\beta E} = \int dE\, \Omega(E) e^{-\beta E}$$

Quantum Ensembles

Classical ensemble was a probability distribution in phase space $\rho(q_i, p_i)$ such that averages were

$$\langle X \rangle = \prod_i \int dp_i\, dq_i\, X(q_i, p_i)\, \rho(q_i, p_i)$$

In quantum mechanics, the density function ρ becomes a density operator or density matrix.

In QM, the states of the ~~state~~ system are given by wave functions $|\psi\rangle$. Suppose we ~~hue~~ have a system which we know has probability p_k to be in state $|\psi^k\rangle$. Then the average of some observable would be

$$\langle \hat{X} \rangle = \sum_k p_k \langle \psi^k | \hat{X} | \psi^k \rangle$$

Note this is an incoherent sum. Not a coherent superposition of different states $|\psi^k\rangle$

we define the density ~~matrix as~~ operator as

$$\hat{\rho} = \sum_k |\psi^k\rangle p_k \langle \psi^k|$$

If $\{|n\rangle\}$ are a complete set of basis states (for example the energy eigenstates) then the density matrix is

$$\rho_{nm} = \langle n | \hat{\rho} | m \rangle = \sum_k \langle n | \psi^k \rangle p_k \langle \psi^k | m \rangle$$

Note:

$$\rho_{nm}^* = \sum_k \langle \psi^k | n \rangle p_k \langle m | \psi^k \rangle \qquad p_k \text{ is } \underline{\text{real}}$$

$$= \sum_k \langle m | \psi^k \rangle p_k \langle \psi^k | n \rangle = \rho_{mn}$$

So

$$\rho_{nm}^* = \rho_{mn} \Rightarrow \hat{\rho} \text{ is Hermitean}, \ \hat{\rho} = \hat{\rho}^\dagger$$

$$\Rightarrow \hat{\rho} \text{ can be diagonalized}$$

For the average of any observable

$$\langle \hat{X} \rangle = \sum_k p_k \langle \psi^k | X | \psi^k \rangle$$

$$= \sum_{\substack{k \\ m,n}} p_k \langle \psi^k | n \rangle \langle n | X | m \rangle \langle m | \psi^k \rangle$$

$$= \sum_{m,n} X_{nm} \rho_{mn} = \text{trace}(\hat{X} \hat{\rho})$$

If we take $\hat{X} = \hat{\mathbb{I}}$ identity operator, then we get the normalization condition

$$1 = \text{trace}\, \hat{\rho} = \sum_n \rho_{nn}$$

As for any operator in the Heisenberg picture, its equation of motion is

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{\mathcal{H}}, \hat{\rho}] \qquad \text{quantum analogue of Liouville's eqn}$$

$\Rightarrow$ if $\hat{\rho}$ is to describe a stationary equilibrium, it is necessary that $\hat{\rho}$ commutes with $\hat{H}$, $[\hat{H}, \hat{\rho}] = 0$, so $\partial\hat{\rho}/\partial t = 0$.

$\Rightarrow$ $\hat{\rho}$ is diagonal in the basis formed by the energy eigenstates. If these states are $|\alpha\rangle$ then

$$\langle\alpha|\hat{H}\hat{\rho}|\beta\rangle = E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle$$
$$= \langle\alpha|\hat{\rho}\hat{H}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$\Rightarrow \quad \langle\alpha|\hat{\rho}|\beta\rangle = 0 \quad \text{unless } E_\alpha = E_\beta$$

So $\hat{\rho}$ only couples eigenstates of equal energy (ie degenerate states) but since $\hat{\rho}$ is Hermitian, it is diagonalizeable $\Rightarrow$ we can always take appropriate linear combinations of degenerate eigenstates to make eigenstates of $\hat{\rho}$. In this basis $\hat{\rho}$ is diagonal.

$$\hat{H}|\alpha\rangle = E_\alpha|\alpha\rangle \quad , \quad \hat{\rho}|\alpha\rangle = \rho_\alpha|\alpha\rangle$$

or

$$\langle\alpha|\hat{H}|\beta\rangle = E_\alpha \delta_{\alpha\beta} \quad , \quad \langle\alpha|\hat{\rho}|\beta\rangle = \rho_\alpha \delta_{\alpha\beta}$$

$$\delta_{\alpha\beta} = \begin{cases} 1 & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases} \qquad \text{Kronecker delta}$$

Even though a stationary $\hat{\rho}$ is diagonal in the basis of energy eigenstates, we can always express it in terms of any other complete basis states

$$\rho_{nm} = \langle n|\hat{\rho}|m\rangle = \sum_{\alpha\beta} \langle n|\alpha\rangle\langle\alpha|\hat{\rho}|\beta\rangle\langle\beta|m\rangle$$

$$= \sum_{\alpha} \langle n|\alpha\rangle \rho_{\alpha} \langle\alpha|m\rangle$$

in this basis, $\hat{\rho}$ need not be diagonal

This will be usefull because we may not know the exact eigenstates for $\hat{H}$. If $\hat{H} = \hat{H}^0 + \hat{H}^1$ we might know the eigenstates of the simpler H^0, but not the full $\hat{H}$. In this case it may be convenient to express $\hat{\rho}$ in terms of the eigenstates of $\hat{H}^0$ and treat $\hat{H}^1$ in perturbation. In general it is useful to have the above representation for $\hat{\rho}$ and $\langle\hat{X}\rangle = \mathrm{tr}(\hat{X}\hat{\rho})$ in an operator form that is indep of its representation in any particular basis

Microcanonical ensemble:

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle \rho_{\alpha} \langle\alpha| \quad \text{with } \rho_{\alpha} = \begin{cases} \text{const} & E \le E_{\alpha} \le E+\Delta \\ 0 & \text{otherwise} \end{cases}$$

$$\text{and } \sum_{\alpha} \rho_{\alpha} = 1$$

Canonical ensemble:

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle \rho_{\alpha} \langle\alpha| \quad \text{with } \rho_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{Q_N}$$

$$\text{where } Q_N = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

can also write $Q_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_\alpha \langle\alpha| e^{-\beta \hat{H}} |\alpha\rangle$

$$= \text{trace}\left(e^{-\beta \hat{H}}\right)$$

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Q_N} \qquad \langle \hat{X} \rangle = \frac{\text{tr}\left(\hat{X} e^{-\beta \hat{H}}\right)}{\text{tr}\left(e^{-\beta \hat{H}}\right)}$$

Grand Canonical ensemble

Here $\hat{\rho}$ is an operator in a space that includes wavefunctions with any number of particles N.

$\hat{\rho}$ should commute with both $\hat{H}$ (so it is stationary) and with $\hat{N}$ (so it doesn't mix states with different N)

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathcal{L}}$$

with $\mathcal{L} = \text{trace}\left(e^{-\beta(\hat{H} - \mu\hat{N})}\right) = \sum_{\alpha, N} e^{-\beta(E_\alpha - \mu N)}$

$$\langle \hat{X} \rangle = \frac{\text{tr}\left(\hat{X} e^{-\beta \hat{H}} e^{+\beta\mu\hat{N}}\right)}{\text{tr}\left(e^{-\beta\hat{H}} e^{\beta\mu\hat{N}}\right)}$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle \hat{X} \rangle_N Q_N}{\sum_{N=0}^{\infty} z^N Q_N}$$

Example: The harmonic oscillator

Suppose we have a single harmonic oscillator.
The energy eigenstates are $E_n = \hbar\omega(n + 1/2)$

The canonical partition function will be

$$Q = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n$$

$$Q = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

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

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

We could write

$\langle E \rangle = \hbar\omega(\langle n \rangle + 1/2)$ where $\langle n \rangle$ is the average level of occupation of the h.o.

$$\Rightarrow \langle n \rangle = \frac{1}{e^{\beta\hbar\omega}-1}$$

Quantum Many particle systems

N identical particles described by a wavefunction

$$\psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_N s_N) \qquad \vec{r}_i = \text{position particle } i$$
$$= \psi(1, 2, \dots, N) \qquad s_i = \text{spin of particle } i$$

Indentical particles $\Rightarrow$ prob distribution $|\psi|^2$ should be symmetric under interchange of any pair of coordinates: $|\psi(1,\dots i,\dots, j,\dots N)|^2 = |\psi(1,\dots, j,\dots, i,\dots N)|^2$

$\Rightarrow$ two possible symmetries for ψ

1) ψ is symmetric under pair interchanges
$$\psi(1,\dots, i,\dots, j,\dots, N) = \psi(1,\dots, j,\dots, i,\dots N)$$
2) ψ is antisymmetric under pair interchanges
$$\psi(1,\dots, i,\dots, j,\dots N) = -\psi(1,\dots, j,\dots i,\dots N)$$

(1) = Bose-Einstein statistics - particle called "bosons"
(2) = Fermi-Dirac statistic - particles called "fermions"

For a general permutation $\mathbb{P}$ that interchanges any number of pairs of particles

(1) BE $\Rightarrow$ $\mathbb{P}\psi = \psi$
(2) FD $\Rightarrow$ $\mathbb{P}\psi = (-1)^p \psi$ where p = # pair interchanges
$$= \begin{cases} +\psi & \text{for even permutation} \\ -\psi & \text{for odd permutation} \end{cases}$$

BE statistics are for particles with integer spin, $S = 0, 1, 2, \ldots$
FD statistics are for particles with half integer spin, $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$
(proved by quantum field theory)

Consider <u>non-interacting</u> particles

$$\mathcal{H}(1,2,3,\ldots N) = \mathcal{H}^{(1)}(1) + \mathcal{H}^{(1)}(2) + \cdots \mathcal{H}^{(1)}(N)$$

sum of single particle Hamiltonians

$$\Rightarrow \psi(1,2,\ldots,N) = \phi_1(1)\phi_2(2)\cdots\phi_N(N)$$

where ϕ_i is an eigenstate of single particle $\mathcal{H}^{(1)}$
with energy ϵ_i.

But ψ above does not have proper symmetry.

for BE $\quad \psi_{BE} = \frac{1}{\sqrt{N_P}} \sum_{\mathbb{P}} \mathbb{P}\psi \leftarrow \psi = \phi_1\phi_2\cdots\phi_N$ as above

$\uparrow$ normalization $\qquad \leftarrow$ sum over all permutations $\mathbb{P}$

$N_p = \#$ possible permutations of N particles $= N!$

for FD $\quad \psi_{FD} = \frac{1}{\sqrt{N_P}} \sum_{\mathbb{P}} (-1)^P \mathbb{P}\psi$

You can verify that the above symmetrizing operations give

$$\left\{ \begin{array}{l} \mathbb{P}_0 \psi_{BE} = \psi_{BE} \\ \mathbb{P}_0 \psi_{FD} = (-1)^{P_0} \psi_{FD} \end{array} \right\} \text{ as desired}$$