Fluctuations in $\bar{N}$ and $\bar{E}$ in the grand canonical formalism.

We want to obtain $\overline{(\Delta N)^2} = \overline{N^2} - (\bar{N})^2$

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s} = \mathcal{Z}}$$

$$\left.\frac{\partial \bar{N}}{\partial \alpha}\right|_{\beta, E_s} = -\frac{\sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}} + \frac{\left(\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}\right)^2}{\mathcal{Z}^2} =$$

$$= -\langle N_r^2 \rangle + \langle N_r \rangle^2$$

$$\therefore \overline{(\Delta N)^2} = -\left.\frac{\partial N}{\partial \alpha}\right|_{\beta, E_s} = kT \left.\frac{\partial \bar{N}}{\partial \mu}\right|_{T,V} \quad (1)$$

$$\alpha = -\mu/kT \Rightarrow \frac{1}{d\alpha} = -\frac{kT}{d\mu}$$

Since $n = \frac{N}{V} \Rightarrow v = \frac{V}{N}$ (2)

$$\therefore \frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{\overline{(\Delta N)^2}}{\bar{N}^2} \overset{(1)}{=} \frac{kT}{\bar{N}^2} \left.\frac{\partial \bar{N}}{\partial \mu}\right|_{T,V} \overset{(2)}{=} \frac{kT}{V^2} v^2 \left.\left(\frac{\partial (V/v)}{\partial \mu}\right)\right|_{T,V} =$$

$$= \frac{kT}{V^2} v^2 V \left(-\frac{1}{v^2}\right) \left.\frac{\partial v}{\partial \mu}\right|_T$$

Remember that $E = TS - PV + \mu N$ and $dE = TdS - PdV + \mu dN$ (3)

Since $dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$ (4)

Comparing (3) and (4): $SdT - VdP + Nd\mu = 0$

$$\therefore d\mu = \frac{VdP}{N} - \frac{SdT}{N} = v\,dP - s\,dT \quad \text{if } dT = 0$$

$$\therefore d\mu = v\,dP \quad (5)$$

p eq. of state.

$\therefore\ d\mu = v\, dP$ ⑤

Then
$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{kT}{V^{\cancel{2}}}\, \cancel{v^2 V}\left(-\frac{1}{\cancel{v^2}}\right)\underbrace{\frac{\partial v}{v\,\partial P}\Big|_T}_{\kappa_T:\ \text{isothermal compressibility}} = -\frac{kT}{V}\kappa_T = \overset{\text{eq. of state.}}{-\frac{P}{N}}\kappa_T \propto O(N^{-1})$$

$\therefore$ this means that the fluctuations in $\bar{N}$ are negligible when N is very large.

Now let's look at $\overline{(\Delta E)^2} = \overline{E^2} - (\bar{E})^2 = -\frac{\partial \bar{E}}{\partial \beta}\Big|_{z,V} =$

$$= kT^2 \frac{\partial U}{\partial T}\Big|_{z,V}$$

after some algebra (look in the book) we obtain that

$$\overline{(\Delta E)^2} = \underbrace{\langle (\Delta E)^2 \rangle_{\text{canonical}}}_{\to 0 \text{ as } N\to\infty} + \left(\frac{\partial U}{\partial N}\Big|_{T,V}\right)^2 \underbrace{\overline{(\Delta N)^2}}_{\to 0 \text{ as } N\to\infty}$$

So we see that the fluctuations in $\bar{E}$ are very small too.

— x —

Quick linear algebra refresher

$$\langle \phi | \psi \rangle = (\cdots\cdot)\begin{pmatrix}\vdots\\ \vdots\end{pmatrix} \qquad \text{inner or scalar product.}$$

Ex: (finite vectors in 2D).

$$\langle a|b\rangle = (a_1^*, a_2^*)\begin{pmatrix} b_1 \\ b_2\end{pmatrix} = a_1^* b_1 + a_2^* b_2$$

$|\psi\rangle\langle\phi| = \begin{pmatrix} \cdot \\ \vdots \end{pmatrix} \; \ldots$ outer product

$$|b\rangle\langle a| = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} (a_1^*, a_2^*) = \begin{pmatrix} b_1 a_1^* & b_1 a_2^* \\ b_2 a_1^* & b_2 a_2^* \end{pmatrix} \text{ matrix}$$

Canonical basis: $\hat{e}_1, \hat{e}_2$ $\quad \hat{e}_1 = (1,0)$

$\hat{e}_2 = (0,1)$

$\sum_n |\phi_n\rangle\langle\phi_n| = \mathbb{I}$ $\quad \{|\phi_n\rangle\}$ form a normal basis.

D/(in 2D):

$$|e_1\rangle\langle e_1| + |e_2\rangle\langle e_2| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}(1,0) + \begin{pmatrix} 0 \\ 1 \end{pmatrix}(0,1) =$$

$$= \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_{\text{projects over } \hat{e}_1} + \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}}_{\text{projects over } \hat{e}_2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \equiv \mathbb{I}$$

Consider $\{|n\rangle\}$ orthonormal basis $\Rightarrow \langle n|m\rangle = \delta_{n,m}$

$|a\rangle = \sum_n a_n |n\rangle \qquad |b\rangle = \sum_n b_n |n\rangle$

$\hat{\Omega}$: operator

$\hat{\Omega}|a\rangle = |b\rangle$

$$\therefore \; \hat{\Omega}|a\rangle = \sum_n a_n \hat{\Omega}|n\rangle = |b\rangle = \sum_n b_n |n\rangle \quad (1)$$

Then

$$\langle m|\hat{\Omega}|a\rangle = \sum_n a_n \langle m|\hat{\Omega}|n\rangle =$$

$$= \sum \langle m|\hat{\Omega}|n\rangle a_n \overset{(1)}{=}$$

$$= \sum_n \langle m | \underbrace{\hat{\Omega} | n\rangle}_{b_n|n\rangle} a_n \overset{①}{=}$$

$$= \sum_n b_n \underbrace{\langle m | n \rangle}_{\delta_{m,n}} = b_m$$

$\therefore \quad \langle m | \hat{\Omega} | n \rangle = \Omega_{mn}$ matrix representation of $\hat{\Omega}$ in the $\{|n\rangle\}$ basis.

Then $\sum_n \Omega_{mn} a_n = b_m$ equivalent to $\hat{\Omega}|a\rangle = |b\rangle$

$$\left(\Omega \right) \begin{pmatrix} \vdots \\ a \\ \vdots \end{pmatrix} = \begin{pmatrix} \vdots \\ b \\ \vdots \end{pmatrix}$$

$$\therefore \quad \hat{\Omega} = \sum_{m,n} |m\rangle \, \Omega_{mn} \langle n|$$

D/

$$\langle m' | \hat{\Omega} | n' \rangle = \langle m' | \sum_{m,n} |m\rangle \Omega_{mn} \langle n | n' \rangle =$$

$$= \sum_{m,n} \underbrace{\langle m' | m \rangle}_{\delta_{m,m'}} \Omega_{mn} \underbrace{\langle n | n' \rangle}_{\delta_{n,n'}} =$$

$$= \Omega_{m'n'}$$

Hilbert spaces:

Example: $\hat{r}$: position operator

its eigenvalues (any position in space) define the basis.

$\bar{r}$: eigenvalues

$|\bar{r}\rangle$: eigenvectors

$\langle \bar{r} | \bar{r}' \rangle = \delta(\bar{r} - \bar{r}')$ orthonormal basis.

Definitions:

$$\langle \bar{r} | \psi \rangle \equiv \psi(\bar{r})$$

$$\langle \psi | \bar{r} \rangle \equiv \psi^*(\bar{r})$$

$$\langle \bar{r} | \hat{A} | \psi \rangle = \hat{A}\, \psi(\bar{r})$$

$$\langle \hat{\bar{r}} \rangle = \langle \psi | \hat{\bar{r}} | \psi \rangle = \int_{\text{all space}} \psi^*(\bar{r}) \underbrace{\hat{\bar{r}}\, \psi(\bar{r})}_{\bar{r}\, \psi(\bar{r})} d^3 r =$$

$$= \int_{\text{all space}} \bar{r}\, |\psi(\bar{r})|^2 \, d^3 \bar{r}$$

average value of $\bar{r}$ weighted by the probability $|\psi(\bar{r})|^2$.

Now $\sum_n |\phi_n\rangle \langle \phi_n| = \mathbb{I}$

$$\Downarrow$$

$$\int |x\rangle \langle x| \, dx = 1$$

$\therefore$

$$\langle \psi | \phi \rangle = \langle \psi | \int |x\rangle \langle x| \, dx \, | \phi \rangle =$$

$$= \int \langle \psi | x \rangle \langle x | \phi \rangle \, dx = \int \psi^*_{(x)}\, \phi_{(x)} \, dx$$

and

$$\langle \bar{r} | \psi \rangle = \langle \bar{r} | \int |\bar{r}'\rangle \langle \bar{r}' | \, d\bar{r}' \, | \psi \rangle =$$

$$= \int \underbrace{\langle \bar r | \bar r' \rangle}_{\delta_{r,r'}} \underbrace{\langle \bar r' | \psi \rangle}_{\psi(\bar r')} d\bar r' =$$

$$= \psi(\bar r)$$

Quantum Statistics

Density matrix: quantum equivalent of the density function $\rho(q,p)$

$\mathcal{N} >> 1$ (ensemble members)

$\hat H$ hamiltonian operator.

$\psi(\bar r_i, t)$ is the wave function in coordinate space that defines the state of the ensemble at time t.

$\psi^k(\bar r_i, t)$: $k = 1, \dots, \mathcal{N}$ is the wave function for each ensemble member at time t.

Then:

① $\hat H \psi^k(t) = i\hbar \dot\psi^k(t)$ Schrödinger's eq. is satisfied by each member of the ensemble.

Also

② $\psi^k(t) = \sum_n a_n^k(t) \phi_n$ $\{\phi_n\}$: orthonormal base. (time independent)

Now $\langle \phi_n | \psi^k(t) \rangle = \int \phi_n^* \psi^k(t) \, d\tau \overset{②}{=}$

Now

$$\langle \phi_n | \psi^k(t) \rangle = \int \phi_n^* \psi^k(t)\, d\tau \overset{②}{=}$$

$$= \int \phi_n^* \sum_m a_m^k(t)\, \phi_m \, d\tau =$$

$$= \sum_m a_m^k(t) \underbrace{\int \phi_n^* \phi_m \, d\tau}_{\delta_{n,m}} =$$

$$= a_n^k(t) \qquad ③$$

Notice that the coefficients $a_n^k(t)$ contain all the time dependence of $\psi^k(t)$. Then we want to obtain the equation of motion for $a_n^k(t)$.

From ③

$$a_n^k(t) = \int \phi_n^* \psi^k(t)\, d\tau$$

Then

$$i\hbar\, \dot{a}_n^k(t) = i\hbar \int \phi_n^* \dot{\psi}^k(t)\, d\tau =$$

$$\overset{①}{=} \frac{i\hbar}{i\hbar} \int \phi_n^* \hat{H} \psi^k(t)\, d\tau =$$

$$\overset{②}{=} \int \phi_n^* \hat{H} \sum_m a_m^k(t)\, \phi_m \, d\tau =$$

$$= \sum_m a_m^k(t) \underbrace{\int \phi_n^* \hat{H} \phi_m \, d\tau}_{\langle \phi_n | \hat{H} | \phi_m \rangle \equiv \langle n | \hat{H} | m \rangle \equiv H_{nm}} =$$

$$= \sum_m H_{nm}\, a_m^k(t)$$

$$\therefore \; i\hbar \, \dot{a}_n^k(t) = \sum_m H_{nm} \, a_m^k(t) \qquad (4)$$

From (2) we see that $|a_n^k(t)|^2$ is the probability of finding the system k in eigenstate n at time t.

$$\therefore \; \sum_n |a_n^k(t)|^2 = 1 \qquad \forall k$$

Define: $\hat{\rho}(t)$ such that

$$\rho_{mn}(t) = \frac{1}{N} \sum_{k=1}^{N} a_m^k(t) \, a_n^{*k}(t) = \langle a_m(t) a_n^*(t) \rangle \qquad (5)$$

↳ ensemble average of $a_m a_n^*$

Notice that

$$\rho_{nn}(t) = \langle a_n(t) a_n^*(t) \rangle = \langle |a_n(t)|^2 \rangle$$

is the probability of finding a system chosen at random from the ensemble in state n at time t.

ensemble average of the probability $|a_n(t)|^2$

$$\sum_n \rho_{nn} = \sum_n |a_n(t)|^2 = 1 = \mathrm{tr}\,\hat{\rho}$$

D/

$$\sum_m \rho_{mm} = \sum_m \frac{1}{N} \sum_{k=1}^{N} \{ a_n^k(t) a_n^{*k}(t) \} =$$

$$= \frac{1}{N} \sum_m \sum_{k=1}^{N} |a_n^k(t)|^2 =$$

$$= \frac{1}{N} \sum_{k=1}^{N} \underbrace{\sum_m |a_n^k(t)|^2}_{} = \frac{N}{N} = 1$$

$$= \frac{1}{N}\sum_{k=1}^{N} \underbrace{\sum_{n} |a_n^k(t)|^2}_{1} = \frac{N}{N} = 1$$

Equation of motion for $\hat{\rho}$

Its time dependence will allow us to find the conditions for thermodynamical equilibrium.

$$i\hbar\, \dot{\rho}_{mn}(t) \overset{(5)}{=} i\hbar \frac{1}{N}\sum_{k=1}^{N}\left\{ \dot{a}_m^k(t)\, a_n^{*k}(t) + a_m^k(t)\, \dot{a}_n^{*k}(t)\right\}$$

$$= \frac{1}{N}\sum_{k=1}^{N}\left\{ \sum_j H_{mj}\, a_j^k(t)\, a_n^{k*}(t) - a_m^k(t) \sum_j H_{nj}^{*}\, a_j^{k*}\right\}$$

(4) said that $i\hbar\, \dot{a}_n^k(t) = \sum_m H_{nm}\, a_m^k(t)$

$\therefore\ -i\hbar\, \dot{a}_n^{*k}(t) = \sum_m H_{nm}^{*}\, a_m^{k*}(t) =$

$$\overset{(5)}{=} \sum_j \left(H_{mj}\, \rho_{jn} - \underbrace{H_{nj}^{*}}_{H_{jn}\ (\text{hermiticity of } \hat{H})}\, \rho_{mj} \right) =$$

$$= \sum_j \left(H_{mj}\, \rho_{jn} - \rho_{mj}\, H_{jn} \right) = \left(\hat{H}\hat{\rho} - \hat{\rho}\hat{H} \right)_{mn}$$

$$\therefore\ i\hbar\, \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}] \quad (6)$$

Compare (6) with Liouville's theorem:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

Now $\underbrace{[\rho, H]}_{\text{Poisson's bracket}} \longrightarrow \left(\frac{\hat{\rho}\hat{H} - \hat{H}\hat{\rho}}{i\hbar} \right) = -i\hbar\, \underbrace{[\hat{H}, \hat{\rho}]}_{\text{commutator}}$