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Last time:

Grandcanonical ensemble.

$$\mathcal{Z} = \sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V,T)$$

$$U(z,V,T) = kT^2\left[\frac{\partial}{\partial T} q(z,V,T)\right]$$

$$q = \ln \mathcal{Z}$$

$$F = -kT \ln \mathcal{Z}/z^N$$

Then

$$S = \frac{U-F}{T} = \frac{kT^2}{T}\left[\frac{\partial}{\partial T} q(z,V,T)\right] - \frac{NkT}{T}\ln z + kq$$

Then

$$S = kT\frac{\partial q}{\partial T}\bigg|_{z,V} - Nk\ln z + kq.$$

Examples:

1) Classical ideal gas:

We found that the canonical Z for the ideal gas was given by

$$Z_N(V,T) = \frac{Z_1^N(V,T)}{N!}$$

to take into account the fact that the particles are indistinguishable.

$$Z_1(V,T) = V f(T) \quad \text{(1)}$$

~~the~~ molecule can be anywhere inside V.

Then

$$\mathcal{Z}(z,V,T) = \sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V,T) =$$

$$\overset{(1)}{=} \sum_{N_r=0}^{\infty} \frac{(zVf(T))^{N_r}}{N_r!} = e^{zVf(T)}$$

$$e^x = \sum_{j=0}^{\infty} \frac{x^j}{j!}$$

Then

$$\Omega(z,V,T) = -kT\ln\mathcal{Z} = -kTzVf(T) = -PV$$

Landau potential

also

$$q(z,V,T) = \ln\mathcal{Z} = zVf(T) = \frac{PV}{kT}$$

$$\therefore \quad P = \frac{kT}{V}q = \frac{kT}{\cancel{V}}z\cancel{V}f(T) = kTzf(T) \quad ②$$

Also (see previous lecture)

$$N = z\frac{\partial}{\partial z}q(z,V,T)\Big|_{V,T} = zVf(T) \quad ③$$

$$U = kT^2 \left[\frac{\partial q(z,V,T)}{\partial T}\right|_{z,V} = kT^2 zV \frac{\partial f}{\partial T} \qquad (4)$$

$$F = NkT\ln z - kT\,\underbrace{zVf(T)}_{q} \qquad (5)$$

$$S = \frac{U-F}{T} = kTzVf' - Nk\ln z + kzVf =$$

$$= -Nk\ln z + zVk(Tf' + f) \qquad (6)$$

From (2) and (3) we obtain:

$$z = \frac{P}{kTf} \qquad z = \frac{N}{Vf} \Rightarrow \frac{P}{kT} = \frac{N}{V}$$

or $\boxed{PV = NkT}$

From 3 and 4 we get

$$\frac{N}{Vf} = z = \frac{U}{kT^2Vf'} \Rightarrow U = NkT^2\frac{f'}{f}$$

If $f(T) \propto T^n$ then

$$\boxed{U} = NkT^2 n \frac{T^{n-1}}{T^n} = \frac{NkT^2 n}{T} = \boxed{NkTn}$$

If the gas is non-relativistic $n = 3/2$

$$U = \frac{3}{2}NkT$$

If gas is extremely relativistic $n = 3$

and $U = 3NkT$.

Fluctuations of $\bar{N}$ and $\bar{E}$ in the grand-canonical

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

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

$$+ \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} (+) \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} =$$

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

$\alpha = -\mu/kT$

Then

$$\overline{(\Delta N)^2} = \overline{N^2} - (\bar{N})^2 = -\frac{\partial \bar{N}}{\partial \alpha}\Big|_{\beta,\ \epsilon s} = kT\frac{\partial \bar{N}}{\partial \mu}\Big|_{T,V}$$

Also define $n = \frac{N}{V}$

$v = V/\bar{N} \Rightarrow \bar{N} = \frac{V}{v}$

$$\frac{\overline{(\Delta n)^2}}{(\bar{n})^2} = \frac{\overline{(\Delta N)^2}}{(\bar{N})^2} = \frac{kT}{(\bar{N})^2}\frac{\partial \bar{N}}{\partial \mu}\Big|_{T,V} = \frac{kT v^2}{V^2}\frac{\partial (V/v)}{\partial \mu}\Big|_{T,V} =$$

$$= \frac{kT}{V^{\cancel{2}}} v^2 \cancel{V} \underbrace{\frac{\partial v^{-1}}{\partial \mu}}_{-\frac{1}{v^2}\frac{\partial v}{\partial \mu}}\Big|_{T,V} = -\frac{kT}{V}\frac{\partial v}{\partial \mu}\Big|_{T,V} \quad (7)$$

We need to find a relationship between μ and N:

From first law:

$$dE = T\,dS - P\,dV + \mu\,dN$$

But E is extensive

$$d(\lambda E) = T\,d(\lambda S) - P\,d(\lambda V) + \mu\,d(\lambda N)$$

$$E\,d\lambda + \lambda\,dE = TS\,d\lambda + \lambda T\,dS - PV\,d\lambda - \lambda P\,dV + \mu N\,d\lambda + \lambda\mu\,dN =$$

$$= \lambda\,\big(\overbrace{T\,dS - P\,dV + \mu\,dN}^{dE}\big) + \underbrace{(TS - PV + \mu N)}_{E}\,d\lambda$$

Since $E = TS - PV + \mu N$

then
$$dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

but since we know that $dE = TdS - PdV + \mu dN$

it means that

$$SdT - VdP + Nd\mu = 0$$ constrain

then $$d\mu = \frac{V}{N}dP - \frac{S}{N}dT = v\,dP - s\,dT \quad (8)$$

Going back to (7):

$$\frac{\overline{(\Delta n)^2}}{(\bar{n})^2} = -\frac{kT}{V}\frac{\partial v}{\partial \mu}\Big|_{T,V}$$

since from (8) $d\mu = v\,dP - s\,dT$ if $dT = 0$

$\Rightarrow d\mu = v\,dP$ $\Rightarrow$

$$\frac{\overline{(\Delta n)^2}}{(\bar{n})^2} = -\frac{kT}{V}\frac{\partial v}{v\,\partial P}\Big|_{T,V} = -\frac{kT}{V}K_T = -\frac{P}{N}K_T \sim O\left(\frac{1}{N}\right)$$

K_T : isothermal compressibility (intrinsic).

The fluctuations $\to 0$ when $N \to \infty$.

$$\overline{(\Delta E)^2} = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial \bar{E}}{\partial \beta}\Big|_{z,V} = kT^2 \frac{\partial U}{\partial T}\Big|_{z,V} \qquad (9)$$

$$U \equiv \bar{E}$$

but

$$\frac{\partial U}{\partial T}\Big|_{z,V} = \frac{\partial U}{\partial T}\Big|_{N,V} + \frac{\partial U}{\partial N}\Big|_{T,V} \frac{\partial N}{\partial T}\Big|_{z,V} \qquad (10)$$

Since

$$N = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\Big|_{\beta,V} \quad \text{and} \quad U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}\Big|_{\alpha,V}$$

$$\frac{\partial N}{\partial \beta}\Big|_{\alpha,V} = \frac{\partial U}{\partial \alpha}\Big|_{\beta,V}$$

$$\left.\frac{\partial N}{\partial \beta}\right|_{\alpha,V} = \left.\frac{\partial U}{\partial \alpha}\right|_{\beta,V}$$

since $\beta = \frac{1}{kT}$ and $\alpha = -\frac{\mu}{kT}$

$$\left.\frac{\partial N}{\partial T}\right|_{\alpha,V} \left.\frac{\partial T}{\partial \beta}\right|_{\alpha,V} = \left.\frac{\partial U}{\partial \mu}\right|_{T,V} \left.\frac{\partial \mu}{\partial \alpha}\right|_{T,V}$$

$$-kT^2 \left.\frac{\partial N}{\partial T}\right|_{z,V} = -k\cancel{T} \left.\frac{\partial U}{\partial \mu}\right|_{T,V}$$

$$\therefore \quad \left.\frac{\partial N}{\partial T}\right|_{z,V} = \frac{1}{T} \left.\frac{\partial U}{\partial \mu}\right|_{T,V} \qquad (11)$$

Plugging (11) in (10) and (10) in (9):

$$\overline{(\Delta E)^2} = kT^2 \left[\underbrace{\frac{\partial U}{\partial T}\Big|_{N,V}}_{C_V} + \frac{\partial U}{\partial N}\Big|_{T,V} \frac{1}{T} \frac{\partial U}{\partial \mu}\Big|_{T,V} \right] =$$

$$= \underbrace{kT^2 C_V}_{\langle (\Delta E)^2 \rangle_{\text{canonical}}} + kT \frac{\partial U}{\partial N}\Big|_{T,V} \underbrace{\frac{\partial U}{\partial \mu}\Big|_{T,V}}_{\frac{\partial U}{\partial N}\big|_{T,V} \frac{\partial N}{\partial \mu}\big|_{T,V}} =$$

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

Vanish when $N \to \infty$.

Quantum Statistics

Density Matrix:

$N >> 1$ ensemble members.

$\hat{H}$ hamiltonian operator

At any time t $\psi(\bar{r}_i, t)$ is the wave function for the ensemble.

Each ensemble member has its own wave function $\psi^k(r_i, t)$ $k: 1, \dots, N$

The ψ^k's obey Schrödinger's equation:

$$\hat{H}\,\psi^k(t) = i\hbar\,\dot{\psi}^k(t) \qquad (1)$$

$$\psi^k(t) = \sum_m a^k_m(t)\,\underbrace{\phi_m}_{\text{time independent}} \qquad (2)$$

ϕ_m: functions in an ortho-normal basis.

since $\int \phi^*_m \phi_n \,\delta\tau = \delta_{m,n}$

$$\int \phi^*_m \psi^k(t)\,d\tau = \sum_m a^k_m(t) \int \underbrace{\phi^*_m \phi_m \,d\tau}_{\delta_{m,n}}$$

$$= a^k_m(t)$$

or

$$a^k_n(t) = \int \phi^*_n \psi^k(t)\,d\tau \qquad (3)$$

Let's find the time evolution of $a_n^k(t)$:

$$i\hbar\, \dot{a}_n^k(t) \overset{(3)}{=} i\hbar \int \phi_n^* \, \dot{\psi}^k(t)\, d\tau \overset{(1)}{=}$$

$$\overset{(1)}{=} \frac{i\hbar}{i\hbar} \int \phi_n^* \hat{H}\, \psi^k(t)\, d\tau \overset{(2)}{=}$$

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

$$= \sum_m a_m^k(t) \underbrace{\int \phi_n^* \hat{H} \phi_m \, d\tau}_{H_{nm} \ (4)} =$$

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

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

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

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

$$\rho_{mn}(t) = \underbrace{\frac{1}{N}\sum_{k=1}^{N}}_{\text{ensemble average}} \left\{ a_m^k(t) \left(a_n^k(t)\right)^* \right\} \qquad (5)$$

Notice that $\rho_{nn}(t)$ is $\langle a_n^k a_n^{k*} \rangle =$

$= \langle |a_n|^2 \rangle$ → ensemble average.

Then $\rho_{nn}(t)$ is the probability that a system chosen at random from the ensemble is in state n at time t ∴

$$\sum_n \rho_{nn} = 1$$

because the system has to be in some of the n states.

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$$\sum_m \rho_{mm} = \sum_m \frac{1}{N} \sum_{k=1}^{N} \left\{ a_m^k(t)\, a_m^{k*}(t) \right\} =$$

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

Let's find the time dependence of $\rho_{mn}(t)$:

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

$$\left. + a_m^k(t)\, \dot{a}_n^{k*}(t) \right\} \overset{(4)}{=} \frac{1}{N} \sum_{k=1}^{N} \left\{ \sum_j H_{mj}\, a_j^k(t)\, a_n^{k*}(t) + \right.$$

$$\left. - a_m^k(t) \sum_j H_{nj}^*\, a_j^{k*} \right\} =$$

$$= \sum_j \left(H_{mj}\rho_{jn} - H^*_{nj}\rho_{mj} \right) =$$

using (5) Hjn (hermitian)

$$= \sum_j \left(H_{mj}\rho_{jn} - \rho_{mj} H_{jn} \right) =$$

$$= \left(\hat{H}\hat{\rho} - \rho \hat{H} \right)_{mn}$$

$$\therefore \; i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}].$$

quantum equivalent of Liouville's theorem.

$$\left[\frac{\partial \rho}{\partial t} = -\{\rho, H\} = -\sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \right].$$