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Grand Canonical Ensemble

Example: classical ideal gas.

Canonical Z was given by

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

to consider the undistinguishability

We knew that

$$Z_1(V,T) = V f(T)$$

Then

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

$$= \sum_{N_r=0}^{\infty} \frac{(z V f(T))^{N_r}}{N_r!} = e^{zVf(T)}$$

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

Then

$$q(z, V, T) = \ln \mathcal{Z} = z V f(T) \equiv \frac{PV}{kT} \quad (I)$$

$$q = \frac{PV}{kT}$$

we found last time that

$$N = z \frac{\partial}{\partial z} q(z,V,T)\Big|_{V,T} = z V f(T) \qquad \text{from } (1)$$

(2)

also we found that

$$U = kT^2 \left[\frac{\partial}{\partial T} q(z,V,T)\right]_{z,V} = kT^2 z V \frac{\partial f}{\partial T} \qquad (3)$$

and we also found

$$F = NkT \ln z - kTq = NkT \ln z - kT z V f(T)$$

(4)

also

$$S = \frac{U-F}{T} = kTzV\frac{\partial f}{\partial T} - Nk \ln z + kzVf(T)$$

$$S = -Nk\ln z + zVk\,(Tf' + f) \qquad (5)$$

$$f' = \frac{\partial f}{\partial T}$$

From (1) and (2)

$$kTzf(T) = P \qquad\qquad N = zVf(T)$$

$$\frac{P}{kTf(T)} = \frac{N}{Vf(T)} \qquad \text{if } f(T) \neq 0 \text{ then}$$

$$\boxed{PV = NkT}$$ equation of state.

independent of the form of $f(T)$.

From ② and ③:

$$N = \mathfrak{Z} V f(T) \qquad U = kT^2 \mathfrak{Z} V f'$$

$$\frac{N}{\cancel{V} f(T)} = \frac{U}{kT^2 \cancel{V} f'} \Rightarrow \boxed{U = NkT^2 \frac{f'}{f}}$$

Notice that in general

$f(T) \propto T^n$ $\begin{cases} n = 3/2 & \text{for non relativistic gas} \\ n = 3 & \text{for ultra-relativistic gas} \end{cases}$

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

$U = \frac{3}{2} NkT$ (for ideal gas) and $U = 3NkT$ for relativistic gas.

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

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

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

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

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

$\alpha = -\mu/kT$

$d\alpha = -d\mu/kT$

$\frac{1}{d\alpha} = -\frac{kT}{\partial}$

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

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

$$= \frac{kT \cancel{V} \cancel{v^2}}{V^{\cancel{2}}} \left(-\frac{1}{\cancel{v^2}} \frac{\partial v}{\partial \mu} \right)_{T,V} = -\frac{kT}{V} \frac{\partial v}{\partial \mu}\bigg|_{T,V}$$

but $d\mu = v\,dP - s\,dT$ $\quad v \to V/N \qquad s \to S/N$

$N\,d\mu = V\,dP - S\,dT$

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

but E is extensive:

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

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

$$\text{Also } dE = T\,dS - P\,dV + \mu\,dN + \underbrace{S\,dT - V\,dP + N\,d\mu}_{0}$$

If $T = \text{constant} \Rightarrow dT = 0 \therefore$

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

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

K_T

$$= -\frac{kT}{V}K_T = -\frac{P}{N}K_T \propto \frac{1}{N}$$

isothermal compressibility
intensive property

Then $\sqrt{\frac{\overline{(\Delta n)^2}}{\bar{n}^2}} \propto \frac{1}{\sqrt{N}}$ and vanishes if $\bar{N}$ is very large.

Note: close to a phase transition N can fluctuate a lot but μ remains fixed which means that while the canonical formalism won't be appropriate the grand canonical will work.

Now let's look at the E fluctuations:

$$\overline{(\Delta E)^2} = \overline{E^2} - (\bar{E})^2 = -\frac{\partial \bar{E}}{\partial \beta}\bigg|_{z,V} = kT^2 \frac{\partial U}{\partial T}\bigg|_{z,V} \quad (1)$$

$U \equiv \bar{E}$

but

use that $z = z(\mu)$, $N = N(\mu)$

$$\frac{\partial U}{\partial T}\bigg|_{z,V} = \frac{\partial U}{\partial T}\bigg|_{N,V} + \frac{\partial U}{\partial N}\bigg|_{T,V} \frac{\partial N}{\partial T}\bigg|_{zV} \quad (2)$$

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

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

since $\beta = 1/kT$

$\alpha = -\mu/kT$

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

$$-kT^2 \frac{\partial N}{\partial T}\Big|_{\alpha, V} = -kT \frac{\partial U}{\partial \mu}\Big|_{T, V}$$

$$\frac{\partial N}{\partial T}\Big|_{z,V} = \frac{1}{T}\frac{\partial U}{\partial \mu}\Big|_{T,V} \qquad (3)$$

Plugging (3) and (2) in (1):

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

$$= kT^2 c_V + kT\frac{\partial U}{\partial N}\Big|_{T,V}\frac{\partial U}{\partial N}\Big|_{T,V}\frac{\partial N}{\partial \mu}\Big|_{T,V} =$$

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

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

and it will go to zero as $1/N$ (very sharp) except at phase transitions if $\overline{(\Delta N^2)}$ is very large.

Quantum Statistics

Density matrix : $\hat{\rho}$

it is the quantum mechanical analogous of $\rho(q,p)$ the density function that told us the number of microstates in phase space inside a volume $d\omega$ around (q,p).

$N >> 1$ ensemble members.

$\hat{H}$ Hamiltonian is an operator.

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

$\psi^k(\bar{r}_i, t) : k = 1, \ldots, N$ (wave function for each member of the ensemble).

① $\hat{H}\psi^k(t) = i\hbar\dot{\psi}^k(t)$ Schrödinger's eq.

(functions of an orthonormal phase)

② $\psi^k(t) = \sum_n a_n^k(t)\,\phi_n$

all the time dependence is here

Notice that

$$a_m^k(t) = \int \phi_m^* \psi^k(t)\, d\tau \qquad (3)$$

volume element in coordinate space

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

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

Now

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

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

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

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

$$= \sum_m H_{nm}\, a_m^k(t) \qquad 4$$

From ② we see that $|a_n^k(t)|^2$ is the probability that the ensemble member k is going to be found in eigenstate n at time t.

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

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

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

ρ_{mn} is the ensemble average $\langle a_m(t) a_n^*(t) \rangle$

Notice that

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

it is the average of the probability $|a_n|^2$.

$\rho_{nn}(t)$ gives as the probability of finding a randomly selected member of the ensemble in eigenstate n at time t.

then

$$\sum_n \rho_{nn} = 1 \equiv \operatorname{tr} \hat{\rho}$$

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

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