④ THE GRAND-CANONICAL ENSEMBLE

We saw that softening the constraint of constant energy was very useful when we left the microcanonical ensemble and used instead the canonical ensemble.

* We can further remove the constraints from the calculation. One such important constraint is the number of particles N. We hardly ever measure N directly in large systems, just as we hardly measure E directly.

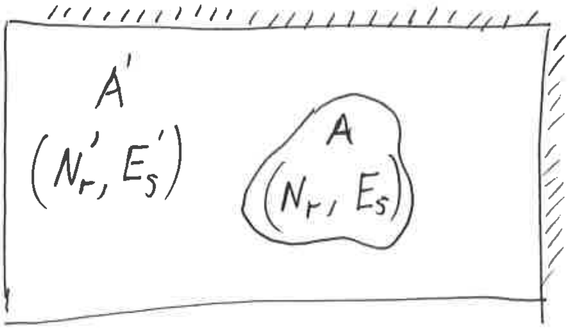
* In the μ-canonical ens. we replaced $E = \text{const.}$ by $\langle E \rangle = \text{const}$, having in mind that in large systems, the fluctuations are relatively small. We will do the same with $N = \text{const}$.

"As usual", we will use two procedures to derive the grand-canonical ensemble, where N and E are both variables.

(i) The sub-system method – a small sub-system immersed in a reservoir

(ii) Distributing N between large number of identical systems.

(4.1) Equilibrium between a system and a particle-energy reservoir



Equilibrium:

$T = T'$

$\mu = \mu'$ (and $P = P'$)

For the combined system:

$$\text{conservation of } E \text{ and } N \left\{ \begin{aligned} N_r + N_r' &= N^{(0)} = \text{const.} \\ E_s + E_s' &= E^{(0)} = \text{const.} \end{aligned} \right.$$

* Since the subsystem is small we can assume

$$\frac{N_r}{N^{(0)}} \ll 1 \quad \text{and} \quad \frac{E_s}{E^{(0)}} \ll 1$$

since the other possibilities are extremely rare.

* The probability that the system is at a macrostate (N_r, E_s) is proportional to the number of microstates of the reservoir

$$P_{r,s} \propto \Omega'(\underbrace{N^{(0)}-N_r}_{N_r'}, \underbrace{E^{(0)}-E_s}_{E_s'})$$

As usual we would like to expand

$$\ln\Omega'(N^{(0)}-N_r, E^{(0)}-E_s) \simeq \ln\Omega'(N^{(0)}, E^{(0)})$$

$$+ \underbrace{\left(\frac{\partial \ln\Omega'}{\partial N'}\right)_{N=N^{(0)}}}_{\left(\frac{\partial S}{\partial N}\right) \;\; -\frac{\mu'}{T'} = -\frac{\mu}{T}} (-N_r) + \underbrace{\left(\frac{\partial \ln\Omega'}{\partial E'}\right)_{E=E^{(0)}}}_{\left(\frac{\partial S}{\partial E}\right) \;\; \frac{1}{T'} = \frac{1}{T}} (-E_s)$$

$$\rightarrow \simeq \ln\Omega'(N^{(0)}, E^{(0)}) + \frac{\mu}{T} N_r - \frac{1}{T} E_s$$

Which implies

$$\boxed{P_{r,s} \propto e^{\frac{\mu}{T} N_r - \frac{1}{T} E_s}}$$

On normalization

$$\boxed{P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r',s'} e^{-\alpha N_{r'} - \beta E_{s'}}}} \qquad \alpha = -\frac{\mu}{T} \qquad \beta = \frac{1}{T}$$

where the summation is over all accessible $N_{r'}, E_{s'}$

④.2 A system in the GC ensemble

* Consider an ensemble of $\mathcal{N}$ identical systems, which share a total number of particles $\mathcal{N}\bar{N}$ and energy $\mathcal{N}\bar{E}$.

$n_{r,s}$ = # systems that have (N_r, E_s)

Then conservation implies

$$\left\{\begin{array}{l} \sum\limits_{r,s} n_{r,s} = \mathcal{N} \\ \sum\limits_{r,s} n_{r,s} N_r = \mathcal{N}\bar{N} \\ \sum n_{r,s} E_s = \mathcal{N}\bar{E} \end{array}\right\}$$

* Any set of numbers $\{n_{r,s}\}$ that obeys represents one possible partition. Any such partition can be realized in $W\{n_{r,s}\}$ ways:

$$W\{n_{r,s}\} = \frac{\mathcal{N}!}{\prod\limits_{r,s}(n_{r,s}!)}$$

* The most probable distribution $\{n^*_{r,s}\}$ can be found by maximizing $\ln W$ under the conservation conditions

$$\mathcal{L} = \ln W - \mu\sum_{r,s} n_{r,s} - \alpha\sum_{r,s} n_{r,s} N_r - \beta\sum_{s} n_{r,s} E_s$$

$$\frac{\partial\mathcal{L}}{\partial n_{r,s}} = \frac{\partial}{\partial n_{r,s}}\left\{\ln N! - \sum_{r,s}\ln(n_{r,s}!)\right\} - \mu - \alpha N_r - \beta E_s$$

$$= -\ln n^*_{r,s} - \mu - \alpha N_r - \beta E_s = 0$$

$$\ln n^*_{r,s} = -\mu - \alpha N_r - \beta E_s$$

$$n^*_{r,s} \propto e^{-\alpha N_r - \beta E_s}$$

And the normalization gives

$$\boxed{P_{r,s} = \frac{n^*_{r,s}}{\mathcal{N}} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum\limits_{r',s'} e^{-\alpha N_{r'} - \beta E_{s'}}}} = \frac{\langle n_{r,s} \rangle}{\mathcal{N}}$$

The parameters α and β are determined by the equations:

$$\bar{N} = \frac{\sum\limits_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum\limits_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \alpha}\left\{ \overbrace{\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}}^{\equiv q} \right\}$$

$$\bar{E} = \frac{\sum\limits_{r,s} E_s e^{-\alpha N_r - \beta E_s}}{\sum\limits_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \beta}\left\{ \ln \sum_{r,s} e^{-\alpha N_r - \beta E_s} \right\}$$

(4.3) Physical significance of the GC ensemble

As usual we start from the sum (actually its log)

$$q = \ln\left\{ \sum_{r,s} e^{-\alpha N_r - \beta E_s} \right\}$$

q is a function of α, β and the energies E_s.

Its differential is $dq = -\bar{N}\,d\alpha - \bar{E}\,d\beta - \sum\limits_s \overset{dE_s}{\sum\limits_r} \cdot \beta \cdot \frac{\langle n_{r,s} \rangle}{\mathcal{N}}$

or $$dq = -\bar{N}\,d\alpha - \bar{E}\,d\beta - \frac{\beta}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, dE_s$$

$$dX = d(\overbrace{q + \alpha\bar{N} + \beta\bar{E}}^{X}) = dq + d(\alpha\bar{N}) + d(\beta\bar{E})$$

$$= \alpha\, d\bar{N} + \beta\, d\bar{E} - \frac{\beta}{\mathcal{N}} \sum \langle n_{r,s} \rangle \, dE_s$$

$$= \beta \left[\frac{\alpha}{\beta}\, d\bar{N} + d\bar{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, dE_s \right]$$

Remember the 1st law of TD

$$\underset{\text{heat}}{\delta Q} = \underset{\substack{\text{energy}\\ \text{change}}}{d\bar{E}} + \underset{\substack{\text{work done}\\ \text{by the system}}}{dW} - \mu\, d\bar{N}$$

We see the correspondence $dX = \beta\, dQ$

with $\dfrac{\alpha}{\beta} = -\mu$ and $dW = -\sum_{r,s} \dfrac{\langle n_{r,s} \rangle}{\mathcal{N}} dE_s$

Together with $\beta = \dfrac{1}{T}$ we find $\alpha = -\mu\beta = -\dfrac{\mu}{T}$

From all this we see $dX = \dfrac{dQ}{T} = dS$

$$q + \alpha\bar{N} + \beta\bar{E} = X = S$$

or $$q = S - \alpha\bar{N} - \beta\bar{E} = \frac{TS + \mu\bar{N} - \bar{E}}{T}$$

But we also know that $G = \bar{E} - TS + PV = \mu\bar{N}$ is the Gibbs energy, such that

$$\Big[\; q = \frac{\cancel{TS} - \cancel{\bar{E}} + (\cancel{\bar{E}} - \cancel{TS} + PV)}{T} = \frac{PV}{T}$$

And finally

$$\boxed{q = \ln\left\{\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\} = \frac{PV}{T}}$$

This is the central relation of the GC ensemble (just like $A = -T\ln Q$ in the C ensemble)

Another quantity of interest is the fugacity

$$z = e^{+\mu/T} = e^{-\alpha}$$

Also, we call the sum $\mathcal{Q} \equiv \sum_{r,s} z^{N_r} e^{-\beta E_s}$

the Grand Partition Function

$$\boxed{\mathcal{Q}(z,V,T) = \sum_{r,s} z^{N_r} e^{-\beta E_s} = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V,T)}$$

Where by definition $Q_0(V,T) \equiv 1$

It may appear that in order to calculate the GPF we need to calculate the PF

In practice, however this is not the case.

Often it is much easier to calculate the GPF $\mathcal{Q}$ than the PF Q (because we can invert the order of summation)

To derive the TD of the GC ens.:

$$\boxed{P = \frac{T}{V}\ln\mathcal{Q}(z,V,T)} = \frac{T}{V}q$$

$$N(z,V,T) = z\left[\frac{\partial}{\partial z}\ln Q(z,V,T)\right]_{V,T} = T\frac{\partial}{\partial \mu}\left[\ln Q(\mu,V,T)\right]_{V,T}$$

$$U(z,V,T) = -\frac{\partial}{\partial \beta}\left[\ln Q(z,V,T)\right]_{z,V} = T^2\frac{\partial}{\partial T}\left[\ln Q(z,V,T)\right]_{z,V}$$

$$\left\{\begin{matrix} P(z,V,T) \\ N(z,V,T)\end{matrix}\right\} \xrightarrow{\text{eliminating } z} \text{Equation of state } P,V,T,N \text{ relationship}$$

$$\left\{\begin{matrix} U(z,V,T) \\ N(z,V,T)\end{matrix}\right\} \xrightarrow{z} U(N,V,T)$$

from which $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$

The Helmholtz free energy is

$$A = N\mu - PV = NT\ln z - T\ln Q(z,V,T)$$

$$z = e^{\mu/T}$$

$$A = -T\ln\frac{Q(z,V,T)}{z^N}$$

Compare to $A = -T\ln Q$ for the canonical ensemble.

Finally

$$S = \frac{U-A}{T} = T\frac{\partial}{\partial T}\ln Q - N\ln z + \ln Q$$

4.4 Some examples:

The real power of the GC ensemble will be seen when we will consider quantum systems and particle interactions.

The following are just demonstrations.

Classical Ideal Gas

When we considered the Canonical ens. we saw

$$Q_N(V,T) = \frac{1}{N!}\left[Q_1(V,T)\right]^N$$

The factor $N!$ comes from indistinguishability

* This is closely related to the nonlocalized nature of the gas particles. They could be equally anywhere.

Hence

$$Q_1(V,T) = V f(T)$$

Therefore the GPF is

$$\mathcal{Q}(z,V,T) = \sum_{N_r=0}^{\infty} z^N \left[V f(T)\right]^N / N! = e^{zVf(T)}$$

and

$$\boxed{q(z,V,T) = z V f(T)}$$

Now the TD derivation

- $P = \frac{T}{V} q = z T f(T)$

$$N = z \frac{\partial}{\partial z} q = z V f(T) = q$$

$$U = T^2 \frac{\partial}{\partial T} q = z V T^2 f'(T)$$

$$A = N T \ln z - T \underbrace{z V f(T)}_{q}$$

$$S = \frac{U-A}{T} = z V T f'(T) - N \ln z + z V f(T)$$

E.O.S

$$\left.\begin{aligned} P &= z T f(T) \\ N &= z V f(T) \end{aligned}\right\} \longrightarrow \frac{P}{N} = \frac{T}{V} \rightarrow \boxed{PV = NT}$$

Energy relation

$$\left.\begin{aligned} N &= zVf(T) \\ U &= zV\,T^2 f'(T) \end{aligned}\right\} = \frac{U}{N} = \frac{T^2 f'(T)}{f(T)}$$

Specific heat

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = N\frac{\partial}{\partial T}\left[T^2 \frac{f'(T)}{f(T)}\right| = N\frac{\partial}{\partial T}\left[T^2 \frac{\partial}{\partial T}\ln f(T)\right]$$

– Simple cases : if $f(T) \propto T^{n}$

$$\frac{U}{N} = T^2\frac{f'(T)}{f(T)} = nT \rightarrow U = nNT$$

and $C_V = N\frac{\partial}{\partial T}\left[T^2\frac{\partial}{\partial T}\ln f(T)\right| = nN$

Since $\boxed{p = \frac{N}{V}T = \frac{1}{V}\left(\frac{U}{n}\right)}$ energy density

(For non-relativistic gas $n = \frac{3}{2}$; relativistic gas $n = 3$)

Finally

$$N = zVf(T)$$

$$A = NT\ln z - TzVf(T) = NT\ln\frac{N}{Vf(T)} - NT$$

$$= NT\left[\ln\frac{N}{Vf(T)} - 1\right]$$

$$S = \frac{1}{T}(U - A) = NT\frac{f'(T)}{f(T)} - N\ln\frac{N}{Vf(T)} + N$$

$$= N\left[\frac{Tf'(T)}{f(T)} - \ln\frac{N}{Vf(T)} + 1\right]$$

* Independent localized particles

(An approximation for non-interacting solid)

This is similar to the case of harmonic oscillators

Now $\quad Q_N(V,T) = [Q_1(V,T)]^N$

Since particles are localized Q_1 does not depend on V.

$$Q_1(V,T) = \phi(T)$$

The GPF is

$$\mathcal{Q}(z,V,T) = \sum_{N_r=0}^{\infty} z^{N_r}[\phi(T)]^{N(r)} = \frac{1}{1-z\phi(T)}$$

$$(z\phi(T) < 1)$$

We start from pressure

$$P = \frac{T}{V}\ln\mathcal{Q} = -\frac{T}{V}\ln[1-z\phi(T)]$$

* Since both z and T are intensive
P vanishes at the TD limit when $V\to\infty$

- The other TD functions

$$N = z\frac{\partial}{\partial z}\ln\mathcal{Q} = \frac{z\phi(T)}{1-z\phi(T)}$$

$$U = T^2\frac{\partial}{\partial T}\ln\mathcal{Q} = T^2\,\frac{z\phi'(T)}{1-z\phi(T)}$$

$$A = -T\ln\frac{\mathcal{Q}}{z^N} = -T\ln\frac{1}{z^N(1-z\phi(T))}$$

$$= T\ln[z^N(1-z\phi(T))] = NT\ln z + T\ln(1-z\phi(T))$$

$$S = \frac{1}{T}(U-A) = T\,\frac{z\phi'(T)}{1-z\phi(T)} - NT\ln z + T\ln(1-z\phi)$$

$$N = \frac{z\phi}{1-z\phi} \longrightarrow N = z\phi(N+1) \longrightarrow z\phi = \frac{N}{N+1} \simeq 1-\frac{1}{N}$$

Therefore $1 - z\phi(T) \simeq 1 - \left(1 - \frac{1}{N}\right) \simeq \frac{1}{N}$

And

$$A = NT \ln z + T \ln\left(1 - z\phi(T)\right)$$

$$= NT \ln\left[\frac{1}{\phi}\left(1 - \frac{1}{N}\right)\right] + T \ln \frac{1}{N}$$

$$= -NT \ln \phi(T) - \cancel{NT \ln \frac{1}{N}} - T \ln N$$

$$\rightarrow \left[\frac{A}{N} = -T \ln \phi(T) + \underbrace{O\left(\frac{\ln N}{N}\right)}_{} \right.$$

$\longrightarrow 0$ in TD limit

Similarly

$$U = T^2 \frac{z\phi'}{1 - z\phi} = T^2 \frac{\overbrace{\left(1 - \frac{1}{N}\right)\frac{1}{\phi}}^{z}}{\underbrace{1/N}_{1 - z\phi}} \phi' = N T^2 \frac{\phi'(T)}{\phi(T)}$$

$$\left[\frac{U}{N} = T^2 \frac{\phi'(T)}{\phi(T)} \right.$$

$$\left[\begin{aligned} \frac{S}{N} &= \frac{1}{T}\left(\frac{U}{N} - \frac{A}{N}\right) = T \frac{\phi'(T)}{\phi(T)} + \ln \phi(T) \\ &= \frac{d}{dT}\left[T \ln \phi(T)\right] \end{aligned} \right.$$

We already calculated the partition functions of classical oscillators $\phi = \underline{Q_1}(V, T) = \frac{T}{\hbar\omega}$

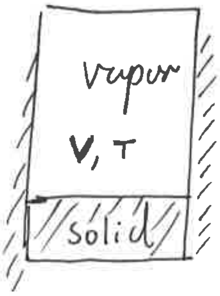
and of QM oscillators

$$\phi = Q_1 = \frac{1}{2\sinh\left(\frac{\hbar\omega}{T2}\right)} \xrightarrow{\text{high} T} \frac{T}{\hbar\omega}$$

For example, for classical oscillators

$$\frac{S}{N} = T \frac{\phi'}{\phi} + \ln \phi = 1 + \ln\left(\frac{T}{\hbar\omega}\right)$$

Example: solid-vapor equilibrium



In equilibrium, the solid and vapor are exchanging particles such that they have the same T, μ (and P)

$\rightarrow$ they have the same fugacity

Now, for an Ideal Gas we saw that

$$[\, N_g = z_g V_g f(T)$$

For the solid phase we saw

$$N_s = \frac{z_s \phi}{1 - z_s \phi} \rightarrow z_s \phi = \frac{N}{N+1} \approx 1$$

$$[\, z_s = \frac{1}{\phi}$$

Since $z_g = z_s \longrightarrow \dfrac{N_g}{V_g f(T)} = \dfrac{1}{\phi} \rightarrow \boxed{\dfrac{N_g}{V_g} = \dfrac{f(T)}{\phi(T)}}$

For gas $\dfrac{P_g}{N_g} = \dfrac{T}{V_g} \longrightarrow \boxed{P_g = \dfrac{N_g}{V_g} T = T \dfrac{f(T)}{\phi(T)}}$

Specifically, we can take monoatomic gas

with $Q_1 = V f(T) \quad f(T) = \dfrac{1}{\lambda^3} \quad \lambda = \dfrac{h}{(2\pi m T)^{1/2}}$

For a 3D "solid" of harmonic oscillators

$$Q_1 = \phi(T) = \left[\frac{1}{2 \sinh\left(\frac{\hbar\omega}{2T}\right)} \right]^3$$

From which we get

$$P_g = T\,\frac{f(T)}{\phi(T)} = T\cdot\frac{(2\pi m T)^{3/2}}{h^3}\left[2\sinh\left(\frac{\hbar\omega}{2T}\right)\right]^3$$

If we also add some cohesion energy for the solid

$$\phi(T) \longrightarrow \phi(T)\,e^{\varepsilon/T} \qquad (\varepsilon > 0)$$

So $$P_g = T\,\frac{(2\pi m T)^{3/2}}{h^3}\left[2\sinh\left(\frac{\hbar\omega}{2T}\right)\right]^3 e^{-\varepsilon/T}$$

For high T

$$P_g \simeq T\,\frac{(2\pi m T)^{3/2}}{h^3}\left(\frac{\hbar\omega}{T}\right)^3 e^{-\varepsilon/T} = \frac{m^{3/2}\,\omega^3}{(2\pi)^{3/2}\,T^{1/2}}\,e^{-\varepsilon/T}$$

[check dimensions $\left[\frac{m^{3/2}\omega^3}{T^{1/2}}\right] = \frac{m^{3/2}\,t^{-3}\cdot t}{m^{1/2}\,\ell} = \frac{m}{t^2\ell} = \frac{E}{V}$]

The condition to get solid is

$$N > N_g = V\,\frac{f(T)}{\phi(T)}$$

Or that the temperature is low enough

$$T < T_c \qquad \text{with} \qquad \boxed{\frac{N}{V} = \frac{f(T_c)}{\phi(T_c)}}$$

characteristic temperature

When two phases appear $N_g(T)$ particles are in vapor, while $N - N_g$ are in solid phase.

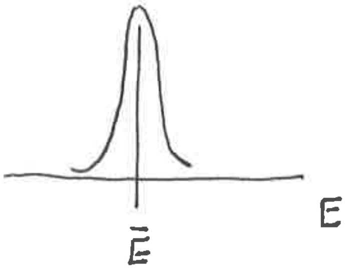
(4.5) Density and Energy fluctuations in GCE

* In the Canonical Ensemble (CE) we saw that we get the same TD as in the μCE, because the energy fluctuations vanish as $\frac{\sqrt{N}}{N} \to 0$.

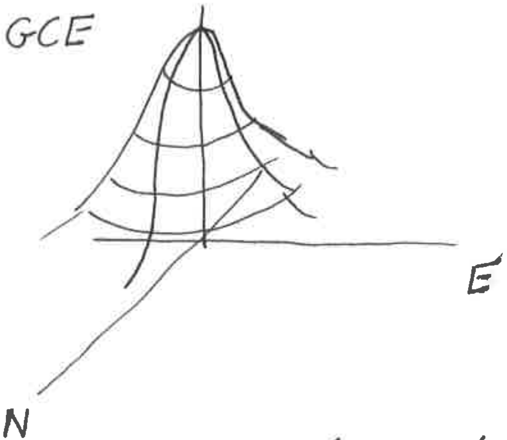
· Similarly, we can show that the number fluctuations also vanish.

μCE N, E

CE



GCE



To see this, consider the average number of particles:

$$\bar{N} = \frac{\sum_{r,s} N_r \, e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \alpha}\right)_{\beta, E_s} = -\left(\frac{\partial \ln Q}{\partial \alpha}\right)$$

$$\left(\frac{d\bar{N}}{\partial \alpha}\right)_{\beta, E_s} = +\frac{1}{Q^2}\left(\frac{\partial Q}{\partial \alpha}\right)\cdot\left(\frac{\partial Q}{\partial \alpha}\right) - \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \alpha^2}\right)$$

$$= +\left(\frac{1}{Q}\frac{\partial Q}{\partial \alpha}\right)^2 - \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \alpha^2}\right) = \bar{N}^2 - \overline{N^2}$$

Therefore,

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

$$\alpha = -\frac{\mu}{T}$$

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The *relative* mean square fluctuation is therefore

$$\frac{\overline{(\Delta N)^2}}{N^2} = \frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{T}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} \qquad \text{where } n = \frac{N}{V}$$

Sometimes it is *useful* to define specific volume

$$v = \frac{V}{\bar{N}} \longrightarrow \bar{N} = \frac{V}{v} \qquad \text{so}$$

$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{Tv^2}{V^2}\cdot\left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} = \frac{Tv^2}{V^2}\cdot V\left(\frac{\partial (1/v)}{\partial \mu}\right)_{T,V}$$

$$= \frac{Tv^2}{V}\cdot\left(-\frac{1}{v^2}\right)\left(\frac{\partial v}{\partial \mu}\right)_{T,V} = \underline{\underline{-\frac{T}{V}\left(\frac{\partial v}{\partial \mu}\right)_T}}$$

From TD we can find $\frac{\partial v}{\partial \mu}$

$$G = U - TS + PV = \mu N$$

$$\cancel{dU} - \cancel{TdS} - SdT + \cancel{PdV} + VdP = \cancel{\mu dN} + d\mu\cdot N$$

1st law $\underline{dU = TdS - PdV + \mu dN}$

$$N d\mu = -SdT + VdP$$

$$\boxed{d\mu = -s\,dT + v\,dP} \qquad s = \frac{S}{N} \quad v = \frac{V}{N}$$

Therefore at constant T $\quad d\mu = v\,dP$

$$\Rightarrow \frac{\overline{(\Delta n)^2}}{\bar{n}^2} = -\frac{T}{V}\left(\frac{\partial v}{\partial \mu}\right)_T = -\frac{T}{V}\cdot\underbrace{\left[\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)\right]}_{-\kappa_T} = \frac{T}{V}\kappa_T$$

We see that this scales like

$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} \propto \frac{1}{\bar{N}}$$ as usual vanishes when the system is big

isothermal compressibility ≡ relative volume change

The only exception is at phase transitions when the compressibility diverges. $\kappa_T \to \infty$

As for the energy fluctuations

$$\bar{E} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{z,V}$$

$$\overline{(\Delta E)^2} = -\left(\frac{\partial \bar{E}}{\partial \beta}\right) = \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \beta^2}\right) - \left[\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)\right]^2 = \overline{E^2} - \bar{E}^2$$

$$\overline{(\Delta E)^2} = -\left(\frac{\partial U}{\partial T}\right)\left(\frac{\partial T}{\partial \beta}\right) = T^2\left(\frac{\partial U}{\partial T}\right)_{z,V}$$

$$\beta = \frac{1}{T} \qquad \frac{\partial \beta}{\partial T} = -\frac{1}{T^2}$$

Note that this is not $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$

$$\left(\frac{\partial U}{\partial T}\right)_{z,V} = \overbrace{\left(\frac{\partial U}{\partial T}\right)_{N,V}}^{= C_V} + \left(\frac{\partial U}{\partial N}\right)_{T,V} \overset{?}{\left(\frac{\partial N}{\partial T}\right)_{z,V}} \longleftarrow \quad dU = \left(\frac{\partial U}{\partial T}\right)_{N,V} dT + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN$$

From

$$\underbrace{N = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \alpha}\right)_{\beta,V} \; ; \quad U = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{\alpha,V}}$$

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

$$\left(\frac{\partial N}{\partial T}\right)_{\alpha,V} \underbrace{\left(\frac{\partial T}{\partial \beta}\right)}_{-\frac{1}{T^2}} = \left(\frac{\partial U}{\partial \mu}\right) \underbrace{\left(\frac{\partial \mu}{\partial \alpha}\right)}_{-\frac{1}{T}} \rightarrow \left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial U}{\partial \mu}\right)_{T,V}$$

Finally we find

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

Or using the result for $\overline{(\Delta N)^2}$

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

$$\boxed{\overline{(\Delta E)^2} = \underset{\substack{\uparrow \\ =\overline{(\Delta E)^2}_{\text{canonical}}}}{T^2 C_V} + \left(\frac{\partial U}{\partial N}\right)^2_{T,V}\overline{(\Delta N)^2}}$$

* The GCE fluctuations are larger because it has more freedom, of also changing the number.

$$\overline{(\Delta E)^2}_{GCE} \geq \overline{(\Delta E)^2}_{CE}$$

Summary

* GCE

- $P_{r,s} \propto e^{\frac{\mu}{T}N_r - \frac{1}{T}E_s}$
- $Q = \sum_{r,s} e^{\frac{\mu}{T}N_r - \frac{1}{T}E_s}$
- $\frac{PV}{T} = \ln Q \longrightarrow P = \frac{T}{V}\ln Q$

(4.6) Thermodynamic Phase Diagrams

- Materials exist in a variety of phases, which depend on pressure, temperature, electric and magnetic field....

- TD and Stat Mech can determine the physical properties and the transitions between the phases.

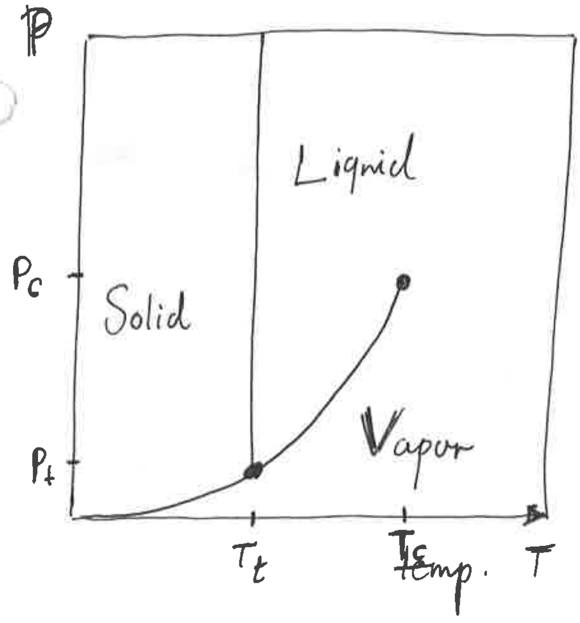
* Thermodynamic Phases are regions of phase space where TD properties are analytic functions of the TD parameters.

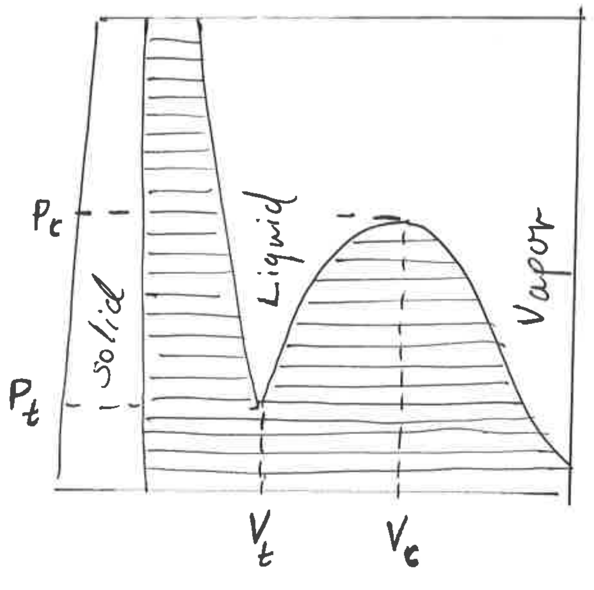
* Phase Transitions occur where the functions are non-analytic.

Analytic function can be expanded as a power series $f(x) = \sum_{n=0}^{\infty} a_n (x-x_0)^n$ for all $x \in N(x_0$

We will focus on phases and phase transitions

Let's look at the example of Argon which is a type of phase diagram we see in many materials.

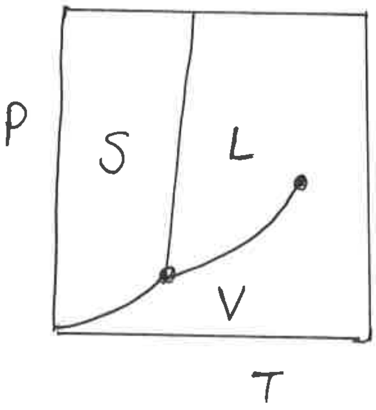




* Moderat ~~T~~ and P: three phases S, L, V

* High T, P: supercritical fluid - smoothly connects L and V

* S-L coexistenc; L-V coexistence; S-V coexistence → Triple point



For Argon:

Triple point $T_t = 83.8\,^\circ K$ $P_t = 68.9\,KPa$

Critical point $T_c = 150.7\,^\circ K$ $P_c = 4.86\,MPa$

(1 atmosphere $\simeq 10^5$ Pa)

* In the P-V diagram the coexistence lines open into areas where both phases coexist.

<u>Tie lines</u> connect the coexisting phases at a given temperature

T ↓

S-V lines - sublimation lines between vapor and solid.

Triple point - connects S-L-V

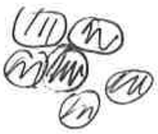
S-L line with L-V lines

critical point L = V

S-L line

Properties of phases

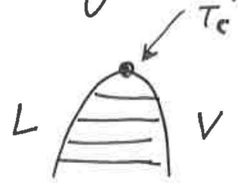
- Vapor : Low-density gas that is approximately ideal
  $PV = NT$, with small corrections due to interaction
- Liquid: High density with strong interactions
  Strong interactions between atoms
  Short-range order.



- Solid Ordered crystal with
  long-range order.

- * All TD properties in a single phase are analytic functions of the parameters (for example $\rho(P,T)$ the equation-of-state)
- * Phase transitions occur when the functions are non-analytic.
- * At coexistence lines the density is discontinuous as we see from the tie lines in the P-V diagrams.
- * In general, all <u>densities</u> such as $\frac{V}{N}, \frac{U}{N}, \frac{S}{N}$ are discontinuous.

- The liquid-vapor coexistence line extends from the triple point to the critical point.
- The discontinuity of the volume/density disappears at the critical point



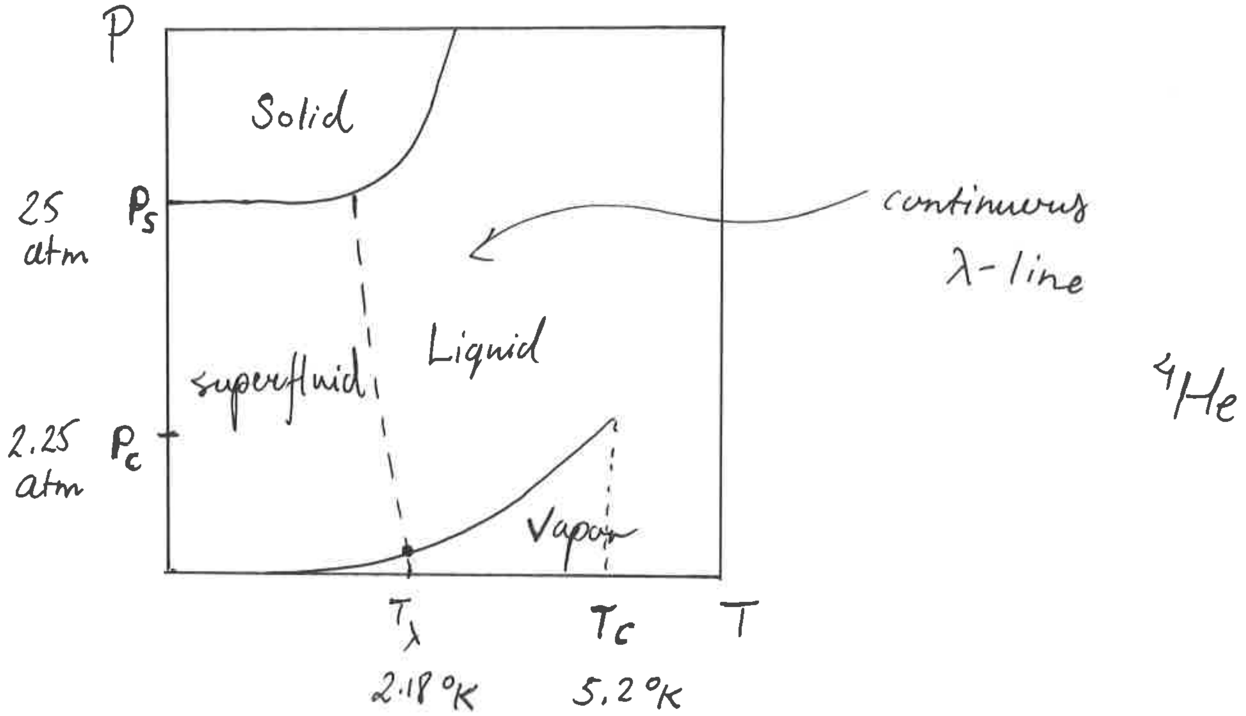
- For this reason critical points are called <u>continuous transitions</u> or <u>second-order phase</u> transitions
- At the critical point the correlation length diverges.

While we can derive the phase diagram of Argon from classical Stat-Mech, at <u>low temperatures</u> there are strong quantum effects.

Quantitatively this happens when

thermal deBroglie length $\left.\right\}$ $$\lambda = \frac{h}{\sqrt{2\pi m T}} \approx n^{-1/3}$$ $\left\{\right.$ distance between molecules

A famous example is liquid helium at temperatures of a few °K



<u>Similar</u>: L-V line that end at T_c

<u>Different</u> S-L does not meet L-V line (no T_t)

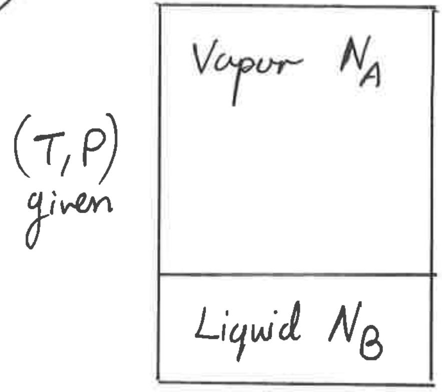
<u>Superfluid</u> zero viscosity
macroscopic quantum coherence.
(^3He doesn't have superfluid)

(4.7) Phase Equilibrium and Clausius-Clapeyron Equation

* The quantity that determines the geometry of the phase diagram is the Gibbs free energy:

$$G(N,P,T) = U - TS + PV = \mu N$$

* Chemical potential $= \dfrac{G}{N}$ Gibbs energy / molecule



Consider a cylinder containing
(A) Vapor + (B) Liquid

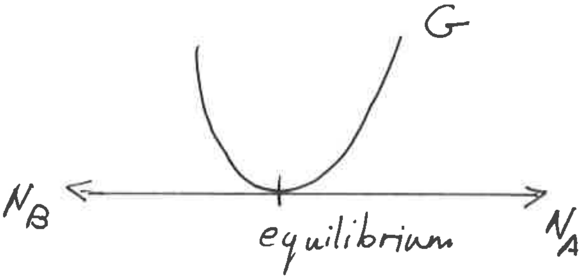
$N = N_A + N_B$ total # of molecules.

Total Gibbs energy:

$$G = G_A(N_A, P, T) + G_B(N_B, P, T)$$

At equilibrium:

Gibbs energy is minimized as the phases exchange particles

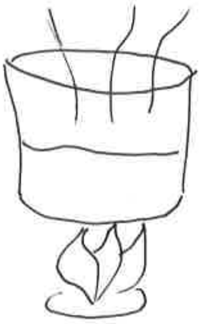


$$dG = \left(\frac{\partial G_A}{\partial N_A}\right)_{T,P} dN_A + \left(\frac{\partial G_B}{\partial N_B}\right)_{T,P} \overset{-dN_A}{dN_B} = (\mu_A - \mu_B)\, dN_A = 0$$

$$\Rightarrow \boxed{\mu_A = \mu_B}$$

<u>Example:</u> consider water at the boiling point; P=1atm T=100°C.

- * At this point $\mu_{vapor}(P,T) = \mu_{liquid}(P,T)$
  So we can move particles between Liquid and Vapor without changing G.
- * The combination of liquid/vapor is determined by the amount of heat that is added or taken.
  This is called latent heat of phase transition.
- * For water $L_V = 2{,}260 \frac{kJ}{kg}$



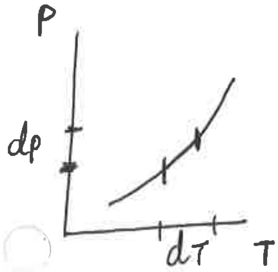
We can find the coexistence curve from the condition of equal chemical potentials

$$\mu_A(P,T) = \mu_B(P,T) \rightarrow$$

a relation between P, T
$P_\sigma(T)$

Along the line $d\mu_A = d\mu_B$

$$\left(\frac{\partial \mu_A}{\partial T}\right)_P dT + \left(\frac{\partial \mu_A}{\partial P}\right)_T dP = \left(\frac{\partial \mu_B}{\partial T}\right)_P dT + \left(\frac{\partial \mu_B}{\partial P}\right)_T dP$$



$$\left(\frac{\partial \mu_A}{\partial T}\right)_P + \left(\frac{\partial \mu_A}{\partial P}\right) \frac{dP_\sigma}{dT} = \left(\frac{\partial \mu_B}{\partial T}\right)_P + \left(\frac{\partial \mu_B}{\partial P}\right)_T \frac{dP_\sigma}{dT}$$

②

definition of $G = U - TS + PV = \mu N$

$$dG = dU - d(TS) + d(PV) = d(\mu N)$$

$$dG = \cancel{dU} - \cancel{TdS} - SdT + \cancel{PdV} + VdP = \cancel{\mu dN} + N d\mu$$

energy conservation $dU = TdS - PdV + \mu dN$

$$-SdT + VdP = N d\mu$$

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\frac{S}{N} \equiv s \quad ; \quad \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{V}{N} \equiv v$$

$$-s_A + v_A \frac{dP_\sigma}{dT} = -s_B + v_B \frac{dP_\sigma}{dT}$$

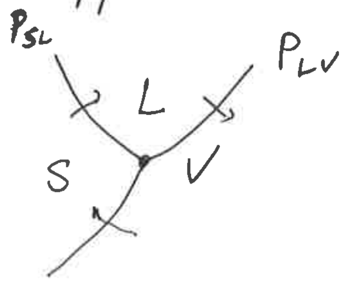
$$s_B - s_A = \frac{dP_\sigma}{dT}(v_B - v_A)$$

Slope of coexistence curve

$$\boxed{\frac{dP_\sigma}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{\Delta S}{\Delta V} = \frac{L_V}{T\Delta V}} \qquad L_V \equiv T\Delta S$$

From this we can determine $P_\sigma(T)$ from the phase transition

What happens at the triple point



$$\mu_S = \mu_L = \mu_V$$

We can apply the C-C relation for each line

$$\Delta S_{LV} = S_L - S_V = \Delta V_{LV} \, P'_{LV}$$

$$\Delta S_{VS} = S_V - S_S = \Delta V_{VS} \, P'_{VS}$$

$$\Delta S_{SL} = S_S - S_L = \Delta V_{SL} \, P'_{SL}$$

$$0 = \Delta V_{LV} P'_{LV} + \Delta V_{VS} P'_{VS} + \Delta V_{SL} P'_{SL}$$

Also $\Delta V_{LV} + \Delta V_{VS} + \Delta V_{SL} = 0$

$$\rightarrow \quad 0 = -(\Delta V_{VS} + \Delta V_{SL}) P'_{LV} + \Delta V_{VS} P'_{VS} + \Delta V_{SL} P'_{SL}$$

$$\left[P'_{LV} = \frac{\Delta V_{VS}}{\Delta V_{VS} + \Delta V_{SL}} P'_{VS} + \frac{\Delta V_{SL}}{\Delta V_{VS} + \Delta V_{SL}} P'_{SL} \right]$$

$$P'_{LV} = \frac{V_V - V_S}{V_V - V_L} P'_{VS} + \frac{V_S - V_L}{V_V - V_L} P'_{SL}$$

⑤ Formulation of Quantum Statistics

* Until now, we have considered:

(A) Classical systems

(B) Quantum systems of distinguishable particles.

* We will see that treating Q systems of indistinguishable particle requires new formalism and brings new physics.

* This new formalism will allow us

- to obtain classical systems as limit of Q systems
- justify to normalization of phase space $\frac{1}{h^{3N}}$

(5.1) QM ensemble theory: density matrix

$\mathcal{N}$ identical QM systems; $\mathcal{N} \gg 1$

$\hat{\mathcal{H}}$ - Hamiltonian operator

$\psi(\bar{r}_i, t)$ - wave function characterize physical state.

$\psi^k(\bar{r}_i, t)$ - physical state of the k-th system.

The evolution of the wave function is determined by the Schrödinger equation

$$\boxed{\hat{\mathcal{H}} \psi^k(t) = i\hbar \dot{\psi}^k(t)} \qquad \text{where } \frac{df}{dt} = \dot{f}$$

We can write the w.f. in a basis (complete orthonormal

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

where the coefficients $a_n^K(t)$ are

$$a_n^K(t) = \int \phi_n^* \psi^K(t)\, dV$$

- the integration is over the coordinate space
- in bra-ket notation $a_n^K(t) = \langle \phi_n | \psi^K(t) \rangle$

$$\psi^K(t) = \sum_n a_n^K(t) | \phi_n \rangle$$

Schrö.

$$i\hbar\, \dot{a}_n^K(t) = \int \phi_n^* \left(i\hbar\, \dot{\psi}^K(t)\right) d\cancel{V}$$

$$= \int \phi_n^* \hat{\mathcal{H}}\, \psi^K(t)\, dV$$

$$= \int \phi_n^* \hat{\mathcal{H}} \left(\sum_m a_m^K(t)\, \phi_m\right) dV$$

$$= \sum_m a_m^K \int \phi_n^* \hat{\mathcal{H}}\, \phi_m\, dV \equiv \sum_m a_m \mathcal{H}_{nm}$$

where we define $\mathcal{H}_{nm} \equiv \int \phi_n^* \hat{\mathcal{H}}\, \phi_m\, dV = \langle \phi_n | \hat{\mathcal{H}} | \phi_m \rangle$

To summarize $\boxed{i\hbar\, \dot{a}_n^K = \sum_m \mathcal{H}_{nm}\, a_m^K}$

As usual in QM, the coefficints a_n^K represent the probability to be in a state n of system K

$|a_n^K(t)|^2 = P_n^K$ and $\sum_n |a_n^K|^2 = 1$.

The density operator

is defined as a matrix ρ with elements

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{K=1}^{\mathcal{N}} a_m^K(t) \left[a_n^K(t)\right]^*$$

this is the ensemble average of $a_m(t)\, a_n(t)^*$.

In particular, the diagonal elements are the average probability $|a_n|^2$

[Note that that is a <u>double</u> average : $|a_n^k(t)|^2$ itself is a propbability and then we take average]

$\rho_{nn}(t)$ is the probability that a randomly chosen system is at state n.

<u>By definition of ρ</u> $\quad \sum_n \rho_{nn} = 1$

Let's see how ρ evolves

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

$$= \frac{1}{N}\sum_{k=1}^{N}\left\{\left[\sum_l H_{ml}\,a_l^k(t)\right]a_n^k(t) - a_m^k(t)\left[\sum_l H_{nl}^*\,a_l^k(t)^*\right]\right\} =$$

$$\boxed{-i\hbar\,\dot{a}_n^{k*} = \sum' H_{nm}^*\,a_m^{k*}}$$

$$H_{nl}^* = H_{ln}$$

$$= \sum_l\left[H_{ml}\,\rho_{ln}(t) - H_{ln}\,\rho_{ml}(t)\right]$$

To summarize

$$i\hbar\,\dot{\rho}_{mn} = \left[\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right]_{m,n}$$

or in matrix form

$$\boxed{i\hbar\,\dot{\hat{\rho}} = [\hat{H},\hat{\rho}]}$$

This is the QM analogue of an equation we already have seen, the Liouville equation.

Reminder:

Liouville's equation is for the density in phase-space $\rho(q,p,t)$:
$$\dot{\rho} = [\rho, H] + \frac{\partial \rho}{\partial t}$$

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

and compare to $\dot{\hat{\rho}} = \frac{[\hat{H}, \hat{\rho}]}{i\hbar}$

- * If the system is at equilibrium, the corresponding ensemble must be stationary $\dot{\rho}_{mn} = 0$.

  This means that:

  (i) $\hat{\rho}$ is an explicit function of $\hat{H}$, $\hat{\rho} = \hat{\rho}(\hat{H})$.

  (ii) The hamitonian must not depend explicitly on time, $\dot{\hat{H}} = 0$.

- * Now if ϕ_n are the eigenfuctions of the Hamiltonian then $H_{mn} = E_n \delta_{mn}$

  and since $\hat{\rho} = \hat{\rho}(\hat{H})$ $\rho_{mn} = \rho_n \delta_{mn}$

  So in this basis both matrices are diagonal.

- * In any other representation, the matrix may not be diagonal, but usually it is symmetric $\rho_{mn} = \rho_{nm}$.

  This comes from the pproperty of detailed blance.

  the forward $m \to n$ tranisition rate is like the reverse $n \to m$.

Finally, we calculate the expectation value of a physical quantity G, represented by the operator $\hat{G}$.

$$\langle G\rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \psi^{k*} G \psi^{k} \, dV = \frac{1}{\mathcal{N}} \sum_{k} \langle \psi_k | G | \psi_k \rangle$$

In terms of the basis ϕ_n

$$\langle G\rangle = \sum_{k=1}^{\mathcal{N}} \sum_{m,n} a_n^{k*} G_{nm} a_m^{k} \quad \text{where } G_{nm} = \int \phi_n^* G \phi_m \, dV$$

$$\left(\text{or} \quad G = \frac{1}{\mathcal{N}} \sum \underbrace{\langle \psi^k | \phi_n \rangle}_{a_n^{k*}} \langle \phi_n | G | \phi_m \rangle \underbrace{\langle \phi_m | \psi^k \rangle}_{a_m} \right)$$

Using the definition of the matrix density $\hat{\rho}_{mn} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^{k} a_n^{k*}$

we find $\langle G\rangle = \sum_{m,n} \rho_{mn} G_{nm} = \sum_{m} (\hat{\rho}\hat{G})_{mm} = \mathrm{Tr}(\hat{\rho}\hat{G})$

$$\boxed{\langle G\rangle = \mathrm{Tr}(\hat{\rho}\hat{G})}$$

* Taking $\hat{G}$ the unity $\hat{G} = \hat{1}$ we have

$$\mathrm{Tr}\,\hat{\rho} = \langle \hat{1} \rangle = 1$$

In general if ψ^{k} the w.f. are not normalized

$$\langle G\rangle = \frac{\mathrm{Tr}(\hat{\rho}\hat{G})}{\mathrm{Tr}(\hat{\rho})}$$

Note: $\langle G\rangle = \mathrm{Tr}(\hat{\rho}\hat{G})$ does not depend on the choice of basis (This is a trace of a matrix)

(5.2) Statistics of various ensembles

Ⓐ The microcanonical ensemble

This ensemble is characterized by

fixed N, fixed V and fixed E

(practically, we can say that it is in $(E - \frac{\Delta}{2}, E + \frac{\Delta}{2})$) with $\Delta \ll E$

$\Gamma(N, V, E; \Delta)$ = # of micro-states.

By assumption, all microstates are equally probable. Accordingly, the density matrix must be diagonal:

$$\rho_{mn} = \rho_n \delta_{mn}$$

with

$$\rho_n = \begin{cases} 1/\Gamma & \text{for each accessible state} \\ 0 & \text{otherwise} \end{cases}$$

As we have shown all TD is derived from the entropy

$$S = \ln \Gamma$$

In a real QM calculation we will not need to introduce a $1/N!$ factor to resolve Gibbs paradox for indistinguishable particles.

In a pure state only one state appears in all systems and $\Gamma = 1$ with $S = \ln\Gamma = 0$.

This means that only one entry in ρ is non-zero

$$\rho = \begin{pmatrix} \ddots & & \\ & 1 & \\ & & 0 \ddots \end{pmatrix} \quad \text{and} \quad \rho^2 = \rho$$

If we write the pure state in a different representation than

$$\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} a_m^k a_n^{k*} = a_m a_n^* \quad \Big\langle \text{same for all } k \text{ systems}$$

and the square matrix is

$$\rho^2_{mn} = \sum_l \rho_{ml} \rho_{ln} = \sum_l a_m a_l^* a_l a_n^*$$

$$= a_m a_n^* \overbrace{\sum_l a_l^* a_l}^{1} = a_m a_n^*$$

In a <u>mixed state</u> $\Gamma > 1$.

To see the properties of $\hat{\rho}$ for a mixed state we need to add another assumption:

<u>Random a priori phase</u> (in addition to equal probabilities) for the probability amplitudes a_n^k.

This implies that the w.f. ψ^k is an <u>incoherent</u> superposition of $\{\phi_n\}$. Thus, in any representation

$$\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} a_m^k a_n^{k*} = \frac{1}{N} \sum_{k=1}^{N} \underbrace{|a_m||a_n|}_{=|a|^2} e^{i(\theta_m^k - \theta_n^k)}$$

$$= |a|^2 \left\langle e^{i(\theta_m^k - \theta_n^k)} \right\rangle = |a|^2 \delta_{mn}$$

We find that ρ continues to be diagonal.

Note that we now used two assumptions ("postulates"):

(1) Equal a priori probability.

(2) Random a priori phase.

Assumption (2) is purely QM: it avoids interference and correlations among systems in the ensemble.

The Canonical Ensemble

Now a macrostate is defined by N, V and T. E is now a variable quantity chosen randomly from an ensemble according to Boltzmann distribution ~ $\exp(-\beta E)$.

The density matrix in the energy representation is therefore

$$\rho_{mn} = \rho_n \delta_{mn}$$

$$\rho_n = \frac{e^{-\beta E_n}}{Q_N(\beta)} \; ; \quad Q_N(\beta) = \sum_n e^{-\beta E_n}$$

with the usual partition function.

We can therefore write

$$\hat{\rho} = \sum_n |\phi_n\rangle \frac{e^{-\beta E_n}}{Q_N(\beta)} \langle \phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} \underbrace{\sum_n |\phi_n\rangle\langle\phi_n|}_{\hat{1}}$$

$$= \frac{e^{-\beta \hat{H}}}{Q_N(\beta)} =$$

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\left(e^{-\beta \hat{H}}\right)}}$$

use the power expansion $e^{-\beta \hat{H}} = \sum_{K=0}^{\infty} \frac{1}{K!} (-\beta \hat{H})^k$

The expectation value of an operator G is

$$\langle G \rangle_N = \mathrm{Tr}(\hat{\rho}\,\hat{G}) = \frac{1}{Q_N(\beta)}\,\mathrm{Tr}\left(e^{-\beta\hat{H}}G\right)$$

$$= \frac{\mathrm{Tr}\left(e^{-\beta\hat{H}}\hat{G}\right)}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

The Grand Canonical Ensemble

In this ensemble $\hat{\rho}$ operates on a space where the number of particles can be any integer ≥ 0. $\hat{\rho}$ must therefore commute with $\hat{H}$ and with the number operator $\hat{n}$ whose eigenvalues are 0, 1, 2... The precise form of the density operator is

$$\hat{\rho} = \frac{1}{Q(\mu, V, T)}\, e^{-\beta(\hat{H} - \mu\hat{n})}$$

with the usual grand partition function

$$Q(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)} = \mathrm{Tr}\left(e^{-\beta(\hat{H} - \mu\hat{n})}\right)$$

The ensemble average of G is

$$\langle G \rangle = \frac{1}{Q(\mu, V, T)}\,\mathrm{Tr}\left(\hat{G}\, e^{-\beta\hat{H}}\, e^{\beta\mu\hat{n}}\right)$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N\, Q_N(\beta)}{\sum_{N=0}^{\infty} z^N\, Q_N(\beta)} \quad \leftarrow$$

$$z = e^{\beta\mu}$$

$$\langle G \rangle_N = \frac{1}{Q_N}\,\mathrm{Tr}\left(e^{-\beta\hat{H}}\hat{G}\right)$$

(5.3) EXAMPLES

(A) Electron in a magnetic field

The electron has intrinsic spin $\frac{1}{2}\hbar\hat{\sigma}$ ($\hat{\sigma}$ Pauli spin operator)

The electron has $J = \frac{1}{2}$ so it has $2J+1 = 2$ states,
up or down $\uparrow\downarrow$

The magnetic field is in the z direction,
so the configurational Hamiltonian is

$$\hat{H} = -\mu_B(\hat{\sigma}\cdot B) = -\mu_B B\hat{\sigma}_z$$

where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton.

and Pauli matrices are

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; ; \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} ; \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The density matrix in the canonical ensemble is

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Tr(e^{-\beta\hat{H}})} = \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}}\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}$$

To calculate $e^{-\beta\hat{A}}$ we can write it as

$$e^{-\beta\hat{H}} = \sum_{k=0}^{\infty}\frac{1}{k!}(-\beta\hat{H})^k = \sum_{k=0}^{\infty}\frac{1}{k!}(\beta\mu_B B)^k(\hat{\sigma}_z)^k$$

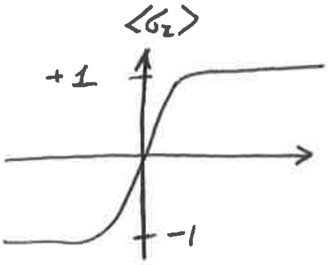
$$(1\ 0)\left(e^{-\beta\hat{H}}\right)\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \sum_{k=0}^{\infty}\frac{1}{k!}(\beta\mu_B B)^k\Big[\underbrace{(\hat{\sigma}_z)_{11}}_{1}\Big]^k = e^{\beta\mu_B B}$$

and so on and so forth

If we want the expectation value of $\hat{\sigma}_z$

$$\langle \sigma_z \rangle = \frac{Tr(\hat{\sigma}\, e^{-\beta\hat{H}})}{Tr(e^{-\beta\hat{H}})} = \frac{1}{Tr(e^{-\beta\hat{H}})}\, Tr\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & -e^{-\beta\mu_B B}\end{pmatrix}$$

$$\langle \sigma_z \rangle = \frac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = tgh(\beta\mu_B B)$$



A particle in a box

A free particle of mass m in a box L^3

The Hamiltanian is

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

with periodic boundary conditions

$$\phi(x,y,z) = \phi(x+L,y,z) = \phi(x,y+L,z) = \phi(x,y,z+L)$$

The general solutions are $\phi_E(\bar{r}) = \frac{1}{L^{3/2}} e^{i\bar{k}\cdot\bar{r}}$

with energy $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

The wave-length that satisfy the B.C. are

$\bar{k} \equiv (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$ with the integer quantum numbers (n_x, n_y, n_z)

We can write $\bar{k} = \frac{2\pi}{L}\bar{n}$ where $\bar{n}$ is a vector $0, \pm 1, \pm 2 ..$

Let us now calculate the density matrix $\hat{\rho}$.

We will use coordinate representation, i.e. wf of $\bar{r}$.

$$\langle \bar{r}| e^{-\beta \hat{H}} |\bar{r}'\rangle = \sum_{E,E'} \langle \bar{r}|E\rangle \underbrace{\langle E| e^{-\beta \hat{H}} |E'\rangle}_{e^{-\beta E}\delta_{EE'}} \langle E'|\bar{r}'\rangle$$

$$= \sum_{E} \underbrace{\langle \bar{r}|E\rangle}_{\phi_E(\bar{r})} e^{-\beta E} \underbrace{\langle E|\bar{r}'\rangle}_{\phi_E^*(r')} = \sum_{E} e^{-\beta E} \phi_E(\bar{r})\, \phi_E^*(\bar{r}')$$

We can now substitute the eigenfunctions $\phi_E(\bar{r}) = \frac{1}{L^{3/2}} e^{i\bar{k}\cdot\bar{r}}$

$$\langle \bar{r}| e^{-\beta \hat{H}} |\bar{r}'\rangle = \sum_{k} e^{-\beta E(k)} \phi_k(\bar{r})\, \phi_k(\bar{r}')^*$$

$$= \frac{1}{L^3} \sum_{k} \exp\left[-\frac{\beta \hbar^2}{2m} k^2 + i\bar{k}\cdot(\bar{r}-\bar{r}') \right]$$

Replace sum by integral $\sum_k \to \left(\frac{L}{2\pi}\right)^3 \int d^3k$ $\longrightarrow$

$$= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \exp\left[-\frac{\beta \hbar^2}{2m} k^2 + i\bar{k}(\bar{r}-\bar{r}') \right] d^3k$$

The integral is the inverse Fourier transform.

$$\mathcal{F}^{-1}[e^{-ak^2}] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-dk^2} e^{-ikr}\, dk = \frac{1}{2\pi^{1/2} d^{1/2}} e^{-\frac{r^2}{4a}}$$

We can write it as a product

$$\langle \bar{r}| e^{-\beta \hat{H}} |\bar{r}'\rangle = \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\alpha k_x^2} e^{ik_x(x'-x)}\, dx \right] \left[\begin{matrix} \text{same for} \\ y \end{matrix} \right] \left[\begin{matrix} \text{same} \\ z \end{matrix} \right]$$

with $\alpha = \frac{\beta \hbar^2}{2m}$

$$= \left(\frac{1}{2\pi^{1/2} \alpha^{1/2}} \right)^3 e^{-\frac{1}{4\alpha} |r-r'|^2}$$

Finally,

$$\langle \bar{r} | e^{-\beta \hat{H}} | \bar{r}' \rangle = \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \exp\left(-\frac{m}{2\beta\hbar^2} |\bar{r} - \bar{r}'|^2 \right)$$

The partition function is

$$\mathrm{Tr}\left(e^{-\beta\hat{H}}\right) = \int d^3r \, \langle \bar{r} | e^{-\beta\hat{H}} | \bar{r} \rangle = \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \int d^3 r$$

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

This is the well-known partition function of single particle $Q_1(\beta)$.

We can now write the density matrix

$$\langle \bar{r} | \hat{\rho} | \bar{r}' \rangle = \frac{\langle \bar{r} | e^{-\beta\hat{H}} | \bar{r}' \rangle}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)} = \frac{1}{V} \exp\left| -\frac{m}{2\beta\hbar^2} |r - r'|^2 \right|$$

- As expected, the density matrix is symmetric $\langle \bar{r} | \hat{\rho} | \bar{r}' \rangle = \langle \bar{r}' | \hat{\rho} | \bar{r} \rangle$.
- Moreover, the diagonal elements are $\langle \bar{r} | \hat{\rho} | \bar{r} \rangle = \frac{1}{V}$. All positions in the box are equally probable.
- The non-diagonal elements represent the probability for $\bar{r} \rightleftarrows \bar{r}'$ transitions.
- The spatial extent of the wave packet is

$$\frac{1}{2\sigma^2} = \frac{m}{2\beta\hbar^2} \longrightarrow \boxed{\sigma = \left(\frac{\beta}{m}\right)^{1/2} \hbar = \frac{\hbar}{(mT)^{1/2}}}$$

This QM vanishes at high-temperature and we get δ- function of a point particle.

Finally, we calculate the expectation value of the Hamiltonian

$$\langle H \rangle = \mathrm{Tr}(\hat{H}\hat{\rho}) = \frac{\mathrm{Tr}(\hat{H}e^{-\beta\hat{H}})}{\mathrm{Tr}(e^{-\beta\hat{H}})}.$$

$$= -\frac{\partial}{\partial\beta}\ln \mathrm{Tr}(e^{-\beta\hat{H}}) = -\frac{\partial}{\partial\beta}\ln\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

$$= -\frac{\partial}{\partial\beta}\left[-\frac{3}{2}\ln\beta\right] = \frac{3}{2}\cdot\frac{1}{\beta} = \frac{3}{2}T$$

Ⓒ Linear Harmonic Oscillator

In the book by Pathria this is calculated in real space representation. Here we will use energy representation

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2q^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2q^2$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, 3\ldots$$

$\phi_n(q)$ are Hermite polynomials

$$\phi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{H_n(\xi)}{(2^n n!)^{1/2}}e^{-\frac{1}{2}\xi^2} \qquad \xi = \left(\frac{m\omega}{\hbar}\right)^{1/2}q$$

However we use the simple energy representation in which

$$\mathrm{Tr}(e^{-\beta\hat{H}}) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega}\cdot\frac{1}{1-e^{-\beta\hbar\omega}} = 1/2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)$$

$$\langle H \rangle = -\frac{\partial}{\partial\beta}\ln Tr(e^{-\beta\hat{H}}) = -\frac{\partial}{\partial\beta}\ln\frac{1}{2\sinh(\frac{1}{2}\beta\hbar\omega)}$$

$$= \frac{\partial}{\partial\beta}\ln\left[2\sinh(\tfrac{1}{2}\beta\hbar\omega)\right] =$$

$$= \frac{2\cosh(\frac{1}{2}\beta\hbar\omega)}{2\sinh(\frac{1}{2}\beta\hbar\omega)} \quad \frac{1}{2}\hbar\omega \cdot \coth\left(\tfrac{1}{2}\beta\hbar\omega\right)$$

The limits :

(i) low T ; $\beta \to \infty$ $\qquad \langle H \rangle = \frac{1}{2}\hbar\omega \leftarrow \coth x \simeq 1$

(ii) high T ; $\beta \to \infty$ $\qquad \langle H \rangle = \dfrac{\frac{1}{2}\hbar\omega}{\frac{1}{2}\beta\hbar\omega} = \dfrac{1}{\beta} = T$

the classical limit

$\coth x \approx \frac{1}{x}$

(5.4) Systems composed of indistinguishable particles

Take N identical particles.

For simplicity assume that they are non-interacting. The the Hamitonian is a sum of single-particle Hamiltonian

$$\hat{H}(p,q) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i)$$

The $\hat{H}_i$ are the same for all particles.

The Schrödinger equation is (time-independenent)

$$\hat{H}\psi_E(\bar{q}) = E\,\psi_E(\bar{q})$$

A straight-forward solution would be:

$$\psi_E(\bar{q}) = \prod_{i=1}^{N} u_{\varepsilon_i}(q_i)$$

where each $u_{\varepsilon_i}(q_i)$ is eigenfunction of $\hat{H}_i$

$$\hat{H}_i u_{\varepsilon_i}(q_i) = \varepsilon_i\, u_{\varepsilon_i}(q_i)$$

and

$$E = \sum_{i=1}^{N} \varepsilon_i$$

* From all this we see that a stationary state may be described in terms of consistuent particles.

In general, we can identify the state by speciting $\{n_i\}$ = # of particles in eigenstate ε_i.

As usual, $$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

Accordingly, the wave-function is

$$\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m) \cdots\cdots$$

Assume, that we apply a permutation of coordinates

$$(1, 2, \ldots N) \longrightarrow (P1, P2 \ldots PN)$$

The resulting wave-function is $P\psi_E(\bar{q})$

$$P\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_{Pm}) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_{Pm}) \cdots\cdots$$

In classical physics particles are <u>distinguishable</u> so permutations of identical particles create new states.

This leads to $\left[\dfrac{N!}{n_1!\, n_2! \ldots} \right.$ states for the partition $\left. \{n_i\} \right]$

Previously we applied Gibbs recipe:

Divide by $N!$ and get $$W_C\{n_i\} = \frac{1}{n_1!\, n_2! \ldots},$$

But in QM this is not enough because even if two particles are in different energy levels it is still physically the same state.

- The whole concept of indexing particles is wrong.
- Only the numbers $\{n_i\}$ matter.

So all permutations which keep $\{n_i\}$ give the same state.

In other words $W_q\{n_i\} = 1$

At the same time, the wave function we previously wrote $\psi_E(\bar{q}) = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m)$

is inappropriate, because when we interchange coordinates between u_i and u_j with $i \neq j$, we get a different form of wave function.

- We therefore need to construct a form of $\psi_E(\bar{q})$ that is insensitive to such changes.
- A simple recipe is to take a combination of all $N!$ w.f.

The combination must have the following property:

$$|P\psi|^2 = |\psi|^2$$

There are two possibilities:

(A) $P\psi = \psi$ for all P

(B) $$P\psi = \begin{cases} +\psi & : P \text{ is an even permutation} \\ -\psi & : P \text{ is an odd permutation} \end{cases}$$

These are called <u>symmetric</u> ψ_S and <u>anti-symmetric</u> ψ_A wave functions.

Their mathematical structure is given by

$$\boxed{\begin{aligned}\psi_S(\bar{q}) &\propto \sum_P P\psi_B(\bar{q}) \\ \psi_A(\bar{q}) &\propto \sum_P \delta_P\, P\,\psi_B(\bar{q})\end{aligned}}$$

where $\psi_B = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=n_1+1}^{n_1+n_2} u_2(q_m) \ldots$ is the product form

and δ_P is the parity of the permutation

$\delta_P = +1$ for even and $\delta_P = -1$ for odd.

We can write the anti-symmetric form using the determinant, which is the anti-symmetric invariant

$$\psi_A(\bar{q}) = \begin{vmatrix} u_i(q_1) & u_i(q_2) & \cdots & u_i(q_N) \\ u_j(q_1) & u_j(q_2) & \cdots & u_j(q_N) \\ \vdots & & & \\ u_\ell(q_1) & u_\ell(q_2) & \cdots & u_\ell(q_N) \end{vmatrix}$$

Slater's determinant

In the determinant we can get the signs through the expansion.

For example:

$$\begin{vmatrix} u_1(q_1) & u_1(q_2) \\ u_2(q_1) & u_2(q_2) \end{vmatrix} = u_1(q_1)u_2(q_2) - u_1(q_2)u_2(q_1)$$

In general, $\det\left|u_i(q_\alpha)\right| = \sum_P \delta_P\, P\,\psi_B(\bar{q})$

(A) When we exchange the arguments of a pair of particles, we exchange the columns of the determinant and it changes sign

$$\begin{vmatrix} u_i(q_1)\ldots & \overset{\downarrow}{u_i(q_\alpha)}\ldots & \overset{\downarrow}{u_i(q_\beta)}\ldots & u_i(q_N) \\ u_j(q_1)\ldots & u_j(q_\alpha)\ldots & u_j(q_\beta)\ldots & u_j(q_N) \\ \vdots & & & \\ u_l(q_1)\ldots & u_l(q_\alpha)\ldots & u_l(q_\beta)\ldots & u_l(q_N) \end{vmatrix}$$

(B) If two particles are in the same single particle state we have two rows that are equal to each other (because the same u_j appears at two rows) and the determinant vanishes.

$\Rightarrow$ A system of indistinguishable particles with <u>anti-symmetric</u> wave-functions has all particles in different single particle states

This is <u>Pauli's Exclusion Principle</u>

---

* The inverse is also true: Particles obeying an exclusion principle are described by an anti-symmetric wave function.

* The particles obey <u>Fermi-Dirac</u> statistics

$$W_{FD}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i^2 = N \\ 0 & \text{if } \sum_i n_i^2 > N \end{cases} \qquad \boxed{\text{Fermions}}$$

Particles that are described by symmetric wave function have no similar restriction and can have any non-negative $\{n_i\}$

These statistics are called Bose-Einstein.

For such BOSONS all such states are equally probable

$$W_{BE}\{n_i\} = 1 \quad \text{for } n_i = 0, 1, 2 \ldots$$

Statistics is linked to spin:

Particles with integral spin (in units of $\hbar$) are bosons

- with half-integral spin are fermions.

Bosons: photons, phonons, gravitons, α particles

Fermion: electrons, protons, neutrons

Our conclusions remain valid also for interacting particles, but still the wave function obeys:

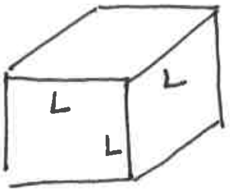
$$P\psi_S = \psi_S$$

$$P\psi_A = \begin{cases} \psi_A & \text{even } P \\ -\psi_A & \text{odd } P \end{cases}$$

The Density matrix and Partition function for free particles

N indisinguishable non-interacting particles.

V volume of the system $= L^3$



In the canonical ensemble

$$\langle r_1 \dots r_N | \hat{\rho} | r_1' \dots r_N' \rangle = \frac{1}{Q_N(\beta)} \langle r_1 \dots r_N | e^{-\beta \hat{H}} | r_1' \dots r_N' \rangle$$

with the partition function:

$$Q_N(\beta) = \mathrm{Tr}\left(e^{-\beta \hat{H}}\right) = \int \langle r_1 \dots r_N | e^{-\beta \hat{H}} | r_1 \dots r_N \rangle \, d^{3N}r$$

Shorthand notation $r_i \to i \; ; \; r_i' \to i'$

$\langle 1 \dots N | \psi_E \rangle = \psi_E(1, \dots N)$ are eigenfunctions with energies E.

We can then expand:

$$\langle 1 \dots N | e^{-\beta \hat{H}} | 1' \dots N' \rangle = \sum_{E,E'} \langle 1 \dots N | \psi_E \rangle \langle \psi_E | e^{-\beta \hat{H}} | \psi_{E'} \rangle \langle \psi_{E'} | 1' \dots N' \rangle$$

$$= \sum_{E,E'} \langle 1 \dots N | \psi_E \rangle \, e^{-\beta E} \delta_{EE'} \langle \psi_{E'} | 1' \dots N' \rangle$$

$$= \sum_E e^{-\beta E} \psi_E(1 \dots N) \, \psi_E^*(1' \dots N')$$

Since particles are non-interacting, we can express the eigenfunctions in terms of single particles and their eigenfunctions $u_i(m)$

The single particle energies are written in terms of the momentum:

$$E = \frac{\hbar^2}{2m} K^2 = \frac{\hbar^2}{2m}\left(\bar{K}_1^2 + \bar{K}_2^2 + \ldots + \bar{K}_N^2\right) = \sum_i \varepsilon_i$$

With periodic boundary conditions

$$u_{\bar{K}}(\bar{r}) = \frac{1}{V^{1/2}} e^{i\bar{K}\cdot\bar{r}} \quad \text{with } \bar{K} = \frac{2\pi}{L}\bar{n}$$

The factor $\frac{1}{V^{1/2}}$ ensures normalization $\int |u_{\bar{K}}(\bar{r})|^2 d\bar{r} = 1$

$\bar{n}$ is a vector of integers $0, \pm 1, \pm 2 \ldots$

The total wave function is then sum of permutation

$$\psi_K(1\ldots N) = (N!)^{-1/2} \sum_P \delta_P \, P\left[u_{K_1}(1) \ldots u_{K_N}(N)\right]$$

where $\delta_P = +1$ if the particles are bosons and $\delta_P = \mathrm{sgn}(P) = \pm 1$ for fermions.

and the total momentum amplitude $K^2 = K_1^2 + \ldots + K_N^2$

When we permute, we can either change the particles or change the momenta $K_1, \ldots K_N$. These will give the same permutations

$$\psi_K(1\ldots N) = (N!)^{-1/2} \sum_P \delta_P \left[u_{K_1}(P1) \ldots u_{K_N}(PN)\right]$$

$$= (N!)^{-1/2} \sum_P \delta_P \left[u_{PK_1}(1) \ldots u_{PK_N}(N)\right]$$

We can now substitute into the density operator

$$\langle 1\ldots N|\, e^{-\beta\hat{H}}\,|1'\ldots N'\rangle = \sum_{E} e^{-\beta E}\,\psi_E(1\ldots N)\,\psi_E^{*}(1'\ldots N')$$

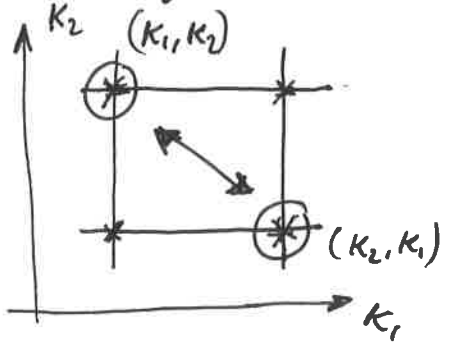
$$= \underbrace{\frac{1}{N!}}_{\text{two } (N!)^{-1/2} \text{ factors}}\ \underbrace{\sum_{K}}_{\text{sum over k instead of } E} e^{-\frac{\beta\hbar^2}{2m}K^2}\Big\{\sum_{P}\delta_P\left[u_{k_1}(P1)\ldots u_{k_N}(PN)\right] \times \sum_{\tilde{P}}\delta_{\tilde{P}}\left[u^{*}_{\tilde{P}k_1}(1')\ldots u^{*}_{\tilde{P}k_N}(N')\right]\Big\}$$

Three comments

(i) The quantity $\{\psi\psi^*\}$ is invariant to permutation of k_i.

(ii) The summation is therefore equivalent to summing the k_i <u>independently</u> and then dividing by $\frac{1}{N!}$

This is equivalent to trying all permutations



(iii) Similarly, the N-fold summation over the k_i all the permutations $\tilde{P}$ will contribut the same.

Therefore we can take only one of them, say $\tilde{P}k_1 = k_1, \ldots\ Pk_n = k_n$, and multiply by $(N!)$

The end result is

$$\langle 1\ldots N|\, e^{-\beta\hat{H}}\,|1'\ldots N'\rangle = \frac{1}{N!}\sum_{k_1\ldots k_N} e^{-\frac{\beta\hbar^2}{2m}(k_1^2+\ldots k_N^2)}$$

$$\times\Big[\sum_{P}\delta_P\left[u_{k_1}(P1)\,u^{*}_{k_1}(1')\right]\ldots\left[u_{k_N}(PN)\,u^{*}_{k_N}(N')\right]\Big]$$

We can now replace all the discrete summation over k_i by integrations $\sum_{k_i} \to \int \frac{L}{2\pi} dk_i$

$$\langle 1 \ldots N | e^{-\beta \hat{H}} | 1' \ldots N' \rangle =$$

$$= \frac{1}{N!} \cdot \frac{1}{(2\pi)^{3N}} \sum_P \delta_P \left[\int \left[e^{-\frac{\beta \hbar^2}{2m} k_1^2 + i k_1 (P1 - 1')} \right] dk_1 \right] \times$$

the L^{3N} cancels with the $\frac{1}{V^{1/2}}$ factors in the $u_i(m)$

$$\ldots \times \left[\int \left[e^{-\frac{\beta \hbar^2}{2m} k_N^2 + i k_N (PN - N')} dk_N \right] \right.$$

Integration is Fourier transform over Gaussian

$$= \frac{1}{(N!)} \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3N/2} \sum_P \delta_P \left[f(P1 - 1') \ldots f(PN - N') \right]$$

where $f(x) = e^{-\frac{m}{2\beta \hbar^2} x^2}$ is the F.T. of Gaussian.

Use the definition of the thermal de Broglie wave length

$\lambda = \frac{h}{(2\pi m T)^{1/2}} = \hbar \left(\frac{2\pi \beta}{m} \right)^{1/2}$ and finally get.

$$\boxed{\langle 1 \ldots N | e^{-\beta \hat{H}} | 1' \ldots N' \rangle = \frac{1}{N! \lambda^{3N}} \sum_P \delta_P \left[f(P r_1 - r_1) \ldots f(P r_N - r_N) \right]}$$

with

$$f(r) = e^{-\pi r^2 / \lambda^2}$$

To calculate the partition function we have to integrate the density matrix:

$$Q_N(\beta) = Tr(e^{-\beta \hat{H}}) = \int dr_1 \ldots dr_N \langle 1 \ldots N | e^{-\beta \hat{H}} | 1 \ldots N^{*} \rangle$$

Before we do that, note that:

(i) The leading term in the summation is when $Pr_i = r_i$ and then we get 1

(ii) The second term will include one pair exchange,
$$f(r_j - r_i) f(r_j - r_i)$$

(iii) The next term will include triplets

So we have

$$\sum_P = 1 \overset{\text{bosons}}{\underset{\text{fermions}}{\pm}} \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} + \ldots$$

where the shorthand is $f_{ij} = f(r_i - r_j)$

Note that the scale of the Gaussian in f is λ, so if the typical distances between the particles are larger, $f \ll 1$.

In other words when $n\lambda^3 = \frac{nh^3}{(2\pi m T)^{3/2}} \ll 1$

the system can be approximated by the first term

This yields $Q_N(\beta) = Tr(e^{-\beta \hat{H}}) =$

Classical Ideal Gas $\longrightarrow$ $= \frac{1}{N! \lambda^{3N}} \int d\vec{r}^{\,3N} \cdot 1 = \frac{V^N}{N! \lambda^{3N}}$

* This shows that we get the the ideal gas partition function from precise QM. Indeed, the Gibbs recipe is correct and originates from the symmetrization of wave functions.

* It also shows that the correspondence between the phase-space integration of classical mechanics over phase space and the summation over the density operator when we divide by cells of volume $\omega_0 = h^{3N}$

The normalized density operator is

$$\langle 1 \dots N | \hat{\rho} | 1' \dots N' \rangle = \frac{1}{Q_N} \langle 1 \dots N | e^{-\beta \hat{H}} | 1' \dots N' \rangle$$

In the classical limit

$$\langle 1 \dots N | \hat{\rho} | 1' \dots N' \rangle = \frac{1}{N! \lambda^{3N}} \Big/ \frac{V^N}{N! \lambda^{3N}} = \frac{1}{V^N}$$

which is a product of N single particle $\frac{1}{V}$ factors since $\langle r | \hat{\rho}_0 | r' \rangle = \frac{1}{V}$

From this we see that in the classical limit there are no correlations between the particles:

However, when the system is genuinely QM and it is degenerate $n\lambda^3 \gtrsim 1$ there could be correlations even if the particles are not interacting through the Hamiltonian.

These purely QM interactions come from the symmetrization of the wave functions.

Of course, these interactions are significant when the inter-particle distance is comparable to λ, $n^{-1/3} \lesssim \lambda$.

We can see this by considering two particles $N=2$.

The summation is now simple

$$\langle r_1 r_2 | e^{-\beta \hat{H}} | r_1 r_2 \rangle = \frac{1}{2!\lambda^6}\left[1 \pm e^{-2\pi \frac{r_{12}^2}{\lambda^2}}\right]$$

So the partition function is

$$Q_2(\beta) = \frac{1}{2\lambda^6}\int\left(1 \pm e^{-2\pi\frac{r_{12}^2}{2}}\right) dr_1\, dr_2$$

$$= \frac{1}{2}\frac{V}{\lambda^6}\left[V \pm \int_0^\infty e^{-2\pi\frac{r^2}{\lambda^2}} 4\pi r^2 dr\right]$$

change coordinates to $\begin{pmatrix} r_1 \\ r_2 \end{pmatrix} \rightarrow \begin{pmatrix} r_1 - r_2 \equiv r \\ r_1 \end{pmatrix}$

$$= \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2\left[1 \pm \frac{1}{2^{3/2}}\left(\frac{\lambda^3}{V}\right)\right] \approx \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2$$

The density operator is therefore (diagonal terms)

$$\langle r_1, r_2 | \hat{\rho} | r_1, r_2 \rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi\frac{r_{12}^2}{\lambda^2}}\right]$$

We see that the probability differs considerably from the classical value $\frac{1}{V^2}$

$$P(r_1,r_2) = \langle r_1 r_2|\hat{\rho}|r_1 r_2\rangle = \frac{1}{V^2}\left[1 \pm \exp\left(-\frac{2\pi r_{12}^2}{\lambda^2}\right)\right]$$

- For bosons $\quad P(r_1 = r_2) = \frac{2}{V^2} \quad$ twice as classical particles

- For fermions $\quad P(r_1 = r_2) = 0 \quad$ Pauli's exclusion

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Sometimes it is useful to describe this QM effect by a classical potential $v_S(r)$.

The relation between correlation functions and potentials give

$$e^{-\beta v_S(r)} = g(r)$$

$$\rightarrow \quad v_S(r) = -\frac{1}{\beta}\ln\left[1 \pm \exp\left(\frac{-2\pi r^2}{\lambda^2}\right)\right]$$