# ④ THE GRAND-CANONICAL ENSEMBLE

We saw that <u>softening the constraint</u> of constant energy was very useful when we left the <u>microcanonical ensemble</u> and used instead the canonical ensemble.
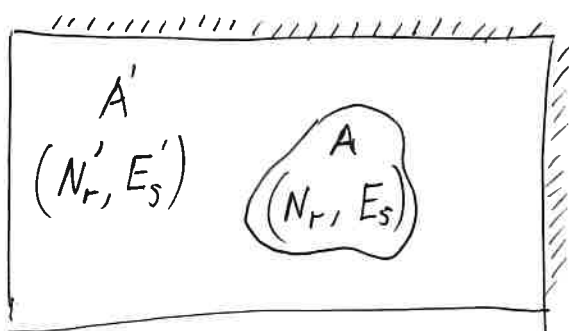
\* We can further remove the constraints from the calculation. One such important constraint is the <u>number of particles N</u>. We hardly ever <u>measure N directly</u> in large systems, just as we hardly measure E directly.

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

"As usual", we will use two procedures to derive the <u>grand-canonical ensemble</u>, 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 <u>Equilibrium between a system and a particle-energy reservoir</u>



Equilibrium:

$$T = T'$$
$$\mu = \mu' \qquad (\text{and } P = P')$$

For the combined system:

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

* 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

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

$$+ \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N=N^{(0)}}(-N_r) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E=E^{(0)}}(-E_s)$$

$$\left(\frac{\partial S}{\partial N}\right) \quad -\frac{\mu'}{T'}=-\frac{\mu}{T} \qquad \left(\frac{\partial S}{\partial E}\right) \frac{1}{T'}=\frac{1}{T}$$

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

Which implies

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

On normalization

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

$$\beta = \frac{1}{T}$$

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 $\mathcal{N}\bar{E}$.

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

Then conservation implies

$$
\begin{cases}
\sum_{r,s} n_{r,s} = \mathcal{N} \\[2mm]
\sum_{r,s} n_{r,s} N_r = \mathcal{N}\bar{N} \\[2mm]
\sum_{r,s} n_{r,s} E_s = \mathcal{N}\bar{E}
\end{cases}
$$

that obeys

\* Any set of numbers $\{n_{r,s}\}$ 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

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

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

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

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

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

And the normalization gives

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

The parameters $\alpha$ and $\beta$ are determined by the equations:

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

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

## (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 $\alpha, \beta$ and the energies $E_s$.

Its differential is $\qquad dq = - \bar{N} d\alpha - \bar{E} d\beta - \sum_s \sum_r \frac{dE_s}{} \cdot \beta \cdot \frac{\langle n_{r,s} \rangle}{\mathcal{N}}$

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

$$dX = d\overbrace{(g + \alpha\bar{N} + \beta\bar{E})} = dg + d(\alpha\bar{N}) + d(\beta\bar{E})$$

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

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

Remember the 1st law of TD

$$\delta Q = d\bar{E} + dW - \mu\,d\bar{N}$$

heat     energy change     work done by the system

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

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

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

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

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

or $\qquad g = S - \alpha\bar{N} - \beta\bar{E} = \dfrac{TS + \mu\bar{N} - \bar{E}}{T}$

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

$$\left[ g = \frac{T\cancel{S} - \cancel{E} + (\cancel{E} - T\cancel{S} + PV)}{T} = \frac{PV}{T}\right.$$

And finally

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

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 <u>fugacity</u>

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

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

the "Grand Partition Function"

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

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

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.:

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

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

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

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

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

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

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 <u>indistinguishability</u>

* This is closely related to the <u>non localized</u> nature of the gas particles. They could be equally <u>anywhere</u>.

Hence

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

Therefore the GPF is

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

and

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

Now the TD derivation

• $P = \dfrac{T}{V} q = z T f(T)$

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

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

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

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

E.O.S
$\left.\begin{array}{l} P = z T f(T) \\[2mm] N = z V f(T) \end{array}\right\} \longrightarrow \dfrac{P}{N} = \dfrac{T}{V} \longrightarrow \boxed{PV = NT}$

Energy relation

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

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     $f(T) \propto T^n$

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

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

$$N = z V f(T)$$

$$A = NT \ln z - T z V f(T) = NT \ln \frac{N}{V f(T)} - NT$$
$$= NT\left[\ln \frac{N}{V f(T)} - 1\right]$$

$$S = \frac{1}{T}(U - A) = NT \frac{f'(T)}{f(T)} - N \ln \frac{N}{V f(T)} + N$$
$$= N\left[\frac{T f'(T)}{f(T)} - \ln \frac{N}{V f(T)} + 1\right]$$

**\* Independent _localized_ particles**

(An approximation for non-interacting solid)

This is similar to the case of harmonic oscillators

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

Since particles are localized $Q_1$ does not depend on $V$.

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

The GPF is

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

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

We start from pressure

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

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

- The other TD functions

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

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

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

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

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

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

Therefore $\quad 1 - z\phi(\tau) \simeq 1 - (1 - \frac{1}{N}) \simeq \frac{1}{N}$

And

$$A = NT \ln Z + T \ln (1 - z\phi(\tau))$$

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

$$= -NT \ln \phi(\tau) - NT \ln N - T \ln N$$

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

$$\underbrace{\phantom{O\left(\frac{\ln N}{N}\right)}}_{} \rightarrow 0 \quad \text{in TD limit}$$

Similarly

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

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

$$\left[ \frac{S}{N} = \frac{1}{T}\left(\frac{U}{N} - \frac{A}{N}\right) = T \frac{\phi'(\tau)}{\phi(\tau)} + \ln \phi(\tau) \right.$$

$$= \frac{d}{d\tau}\left[ T \ln \phi(\tau) \right]$$

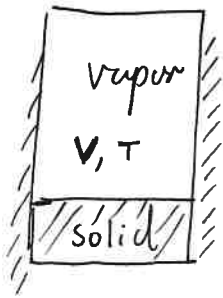We already calculated the partition functions of classical oscillators and of QM oscillators

$$\phi = Q_1(V, T) = \frac{T}{\hbar\omega}$$

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

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 $T, \mu$ (and $P$)

$\rightarrow$ they have the same fugacity

Now, for an Ideal Gas we saw that

$$\left[ N_g = Z_g \, V_g \, f(T) \right.$$

For the solid phase we saw

$$N_s = \frac{Z_s \, \phi}{1 - Z_s \phi} \quad \rightarrow \quad Z_s \phi = \frac{N}{N+1} \approx 1$$

$$\left[ Z_s = \frac{1}{\phi} \right.$$

Since $\quad Z_g = Z_s \quad \rightarrow \quad \frac{N_g}{V_g \, f(T)} = \frac{1}{\phi} \rightarrow \boxed{\frac{N_g}{V_g} = \frac{f(T)}{\phi(T)}}$

For gas $\quad \frac{P_g}{N_g} = \frac{T}{V_g} \quad \rightarrow \quad \boxed{P_g = \frac{N_g}{V_g} T = T \frac{f(T)}{\phi(T)}}$

Specifically, we can take monoatomic gas with $\quad Q_1 = V f(T) \qquad f(T) = \frac{1}{\lambda^3} \qquad \lambda = \frac{h}{(2\pi m T)^{1/2}}$

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 $T$

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

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

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The condition to get solid is

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

Or that the temperature is low enough

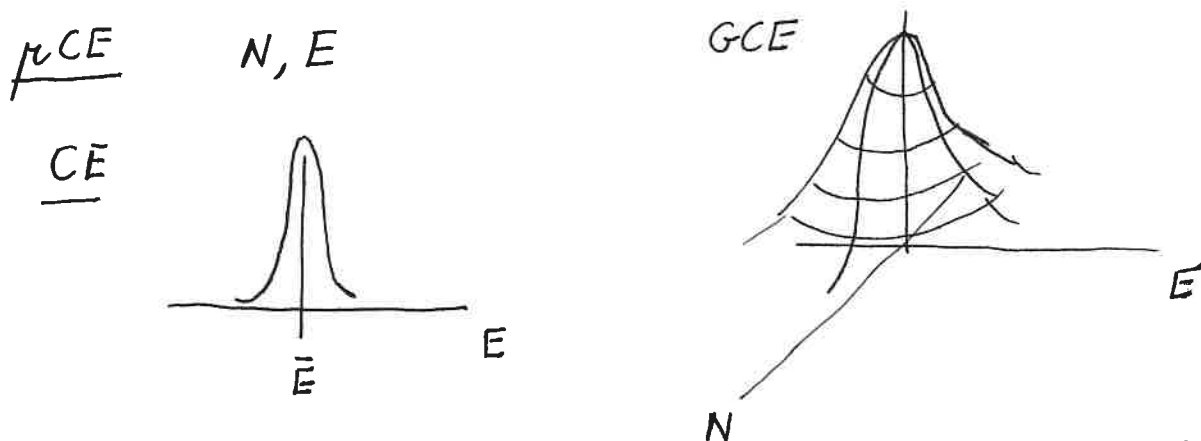$$T < T_c \qquad \text{with} \qquad \boxed{\frac{N}{V} = \frac{f(T_c)}{\phi(T_c)}}$$

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 $\mu$CE,
because the **energy** fluctuations vanish as $\frac{\sqrt{N}}{N} \to 0$.

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

$\mu$CE      N, E

CE



$\bar{E}$   E

GCE



E

N

To see this, consider the average number of particles:

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

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

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

Therefore,

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

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

The relative mean square fluctuation is therefore

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

Sometimes it is useful to define specific volume

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

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

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

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

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

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

1st law

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

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

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

Therefore at constant $T$ $\qquad d\mu = \upsilon\,dP$

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

$$\underbrace{\qquad\qquad}_{-\kappa_T}$$

We see that this scales like

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

isothermal
compressibilty
$\equiv$ relative
volume change

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

As for the energy fluctuations

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

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

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

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

$$\left\{ \begin{array}{l} \beta = \frac{1}{T} \\ \frac{\partial \beta}{\partial T} = -\frac{1}{T^2} \end{array} \right.$$

$$\underbrace{\left(\frac{\partial U}{\partial T}\right)_{Z,V}}_{} = \overbrace{\left(\frac{\partial U}{\partial T}\right)_{N,V}}^{=C_V} + \overbrace{\left(\frac{\partial U}{\partial N}\right)_{T,V}}^{?}\left(\frac{\partial N}{\partial T}\right)_{Z,V}$$

$$\leftarrow \quad dU = \left(\frac{\partial U}{\partial T}\right)_{N,V} dT + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN$$

From

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

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

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

Finally we find

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

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

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

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

$$\uparrow$$

$$= \overline{(\Delta E)^2}_{\text{canonical}}$$

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

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

## 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.
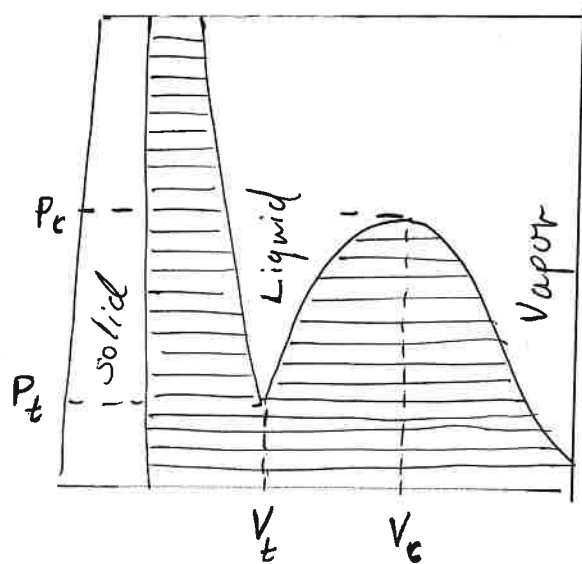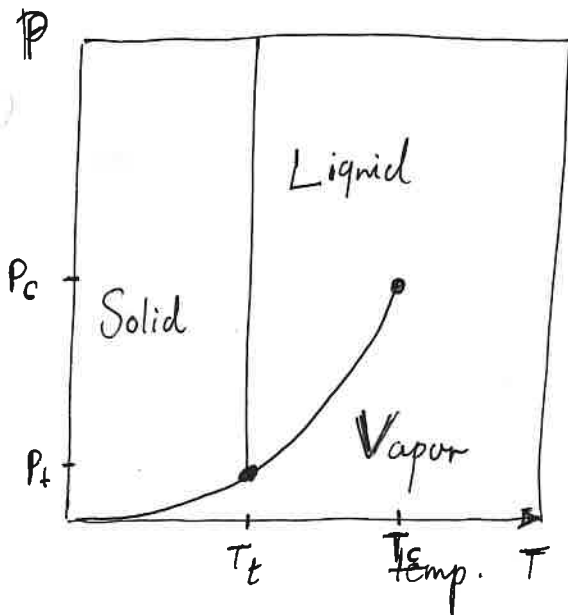
\* __Phase Transitions__ occur where the functions are non-analytic.
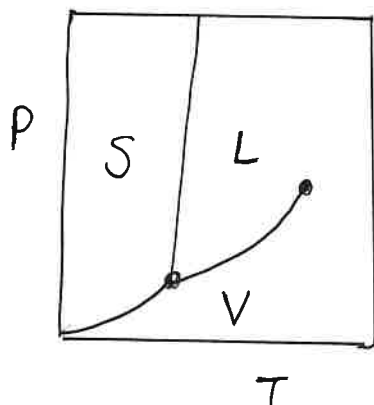
> Analytic function can be expanded as a power series
> $$f(x) = \sum_{n=0}^{\infty} a_n (x-x_0)^n$$ for all $x \in N(x_0$

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    $T_t = 83.8\,°K$   $P_t = 68.9\,KPa$

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

(1 atmosphere $\approx 10^5\,Pa$)

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

Tie lines connect the coexisting phases at a given temperature

S-V lines — <u>sublimation</u> 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

## <u>Properties of phases</u>

• <u>Vapor</u> :   <u>Low-density gas</u> that is approximately <u>ideal</u>

    $PV = NT$ , with small corrections due to interaction

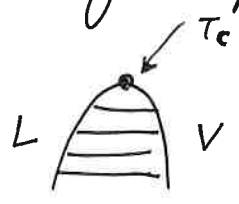• <u>Liquid</u> :   <u>High density</u> with <u>strong interactions</u>

    <u>Strong interactions between atoms</u>

    <u>Short-range</u> order.

• <u>Solid</u>   — Ordered crystal with

    — long-range order.

    — Resists to <u>shear</u>

* 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 <u>discontinuous</u>
  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.

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- The liquid-vapor coexistence line extends
  from the triple point to the critical point.

- The discontinuity of the volume/density disappears
  at the <u>critical point</u>

- For this reason critical points
  are called <u>continuous transitions</u>.

  $\quad$ or $\quad$ <u>second-order phase transitions</u>

- At the critical point the correlation length diverges.

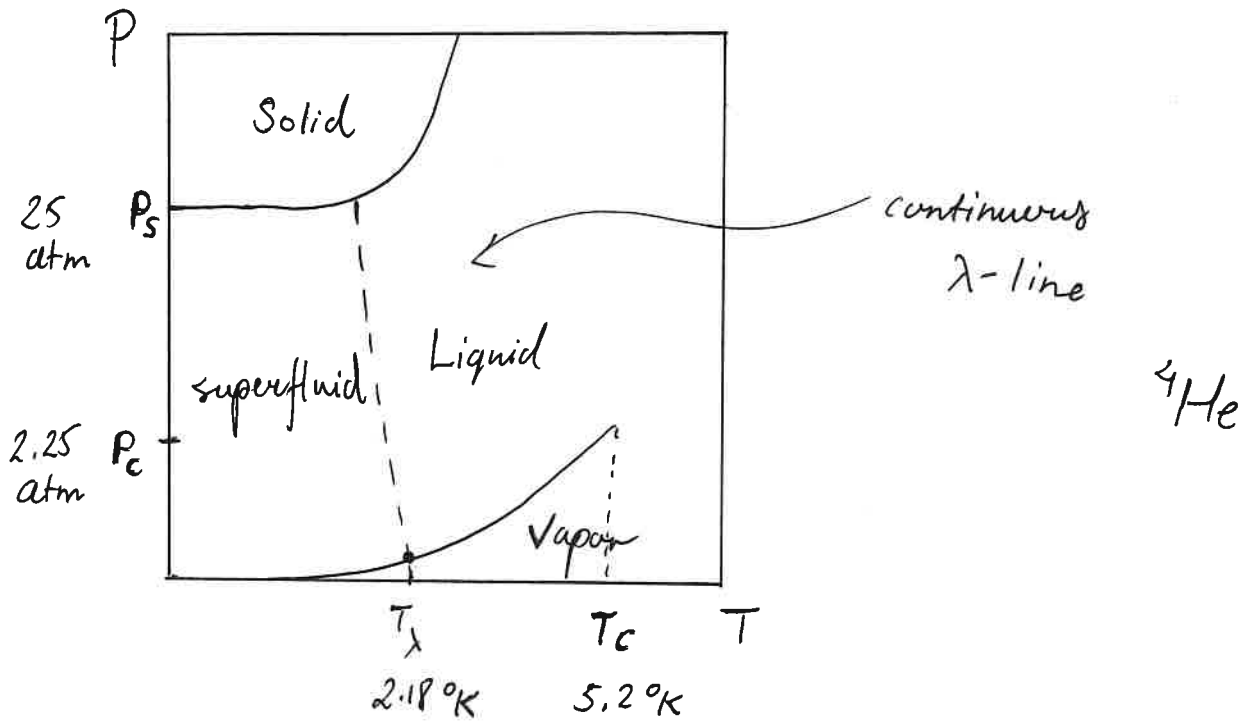$L$ $\quad$ $V$ $\quad$ $T_c$

---

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 $\Big\}$ $\lambda = \dfrac{h}{\sqrt{2\pi m T}} \approx n^{-1/3}$ $\Big\{$ distance
de Broglie $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ between
length $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ molecules

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

P

Solid

25 atm   $P_s$

superfluid    Liquid

2.25 atm   $P_c$

Vapor

$T_\lambda$     $T_c$     T

2.18 °K    5.2 °K

continuous $\lambda$-line

$^4He$

__Similare:__    L-V line that end at $T_c$

__Different__    S-L does not meet L-V line (no $T_t$)

__Superfluid__    zero viscosity
macroscopic quantum coherence.
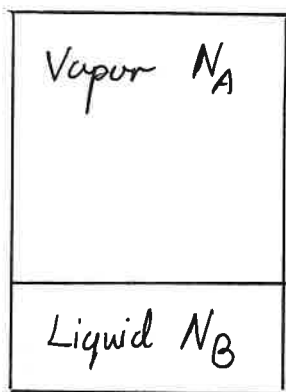( $^3He$ doesn't have superfluid)

(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

Vapor $N_A$

$(T, P)$ given

Liquid $N_B$

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

$$N = N_A + N_B \quad \text{total \# of molecules.}$$

Total Gibbs energy:  $\longrightarrow$ Equivalent to min S

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

At equilibrium:

Gibbs energy is minimized as the phases exchange particles



$N_B \longleftarrow$  equilibrium  $\longrightarrow N_A$   $G$

$-dN_A$

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

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

Example: consider water at the boiling point; $P = 1\,atm\ T = 100°C$.
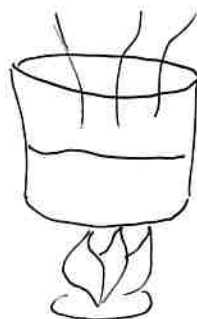
* At this point $\mu_{vapor}(P, T) = \mu_{liquid}(P, T) \Rightarrow P_\sigma(T)$
So we can move particles between Liquid and Vapor without changing $G$.

* 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.

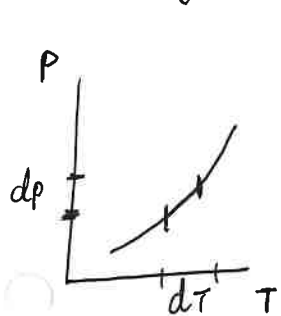* For water  $L_V = 2,260 \dfrac{kJ}{kg}$

(at 1 atm 100 °C)

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

$$\mu_A(P,T) = \mu_B(P,T) \longrightarrow \text{a relation between } P, T \\ P_\sigma(T)$$

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



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

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

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

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

$$dG = \cancel{dU} - T d\cancel{S} - SdT + \cancel{P}dV + VdP = \cancel{\mu dN} + N d\mu$$

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

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

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

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

$$-S_A + \upsilon_A \frac{dP_\sigma}{dT} = -S_B + \upsilon_B \frac{dP_\sigma}{dT}$$

$$S_B - S_A = \frac{dP_\sigma}{dT}(\upsilon_B - \upsilon_A)$$

Slope of coexistence curve

$$\boxed{\frac{dP_\sigma}{dT} = \frac{S_B - S_A}{\upsilon_B - \upsilon_A} = \frac{\Delta S}{\Delta V} = \frac{L_V}{T\Delta V}} \qquad L_V \equiv T\Delta S$$

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

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

$$\Delta S_{US} = S_U - S_S = \Delta U_{US} \, P'_{VS}$$

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

$$\overline{\phantom{XXX}}$$

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

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

$$\longrightarrow \quad 0 = -\left(\Delta U_{US} + \Delta U_{SL}\right) P'_{LV} + \Delta U_{US} P'_{VS} + \Delta U_{SL} P'_{SL}$$

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

$$P'_{LV} = \frac{U_V - U_S}{U_V - U_L} P'_{VS} + \frac{U_S - V_L}{U_V - U_L} P'_{SL}$$