TD 8 Grand Canonical ensemble

8.1) Ideal gas

1) $J(T, \mu, V)$: extensive.

However, T and μ are intensive, the only extensive variable being V

$$\Rightarrow \quad J \propto V$$

$$J(T, \mu, \lambda V) = \lambda J(T, \mu, V) \quad \forall \lambda$$

Take $\lambda = \frac{1}{V} \Rightarrow J(T, \mu, V) = V \, J(T, \mu, 1) = V \, j(T, \mu)$

where $j(T, \mu) = J(T, \mu, 1)$

$\sim$ density of the grand potential $j \sim$ pressure $(-p)$

2) z = single-particle Green function

$$z = \frac{1}{h^3} \int d^3\vec{r} \, d^3\vec{p} \; e^{-\beta \varepsilon(\vec{p})} = \frac{V}{h^3} \int d^3\vec{p} \; e^{-\beta \varepsilon(\vec{p})}, \propto V$$

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} \underbrace{Z_N}_{\text{partition funct}^{\circ} \text{ for } N \text{ particles}}$$

In the Maxwell-Boltzmann approx $Z_N \simeq \frac{z^N}{N!}$

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{z^N}{N!} = \exp\left(z e^{\beta \mu}\right)$$

$$\overline{N}^G = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi = z e^{\beta \mu}$$

$$p^G = \frac{1}{\beta} \frac{\ln \Xi}{V} = -\frac{J}{V} = -j(T, \mu) = \frac{1}{\beta V} z e^{\beta \mu} = \frac{1}{\beta V} \overline{N}^G$$

Therefore $\underline{p^G V = k_B T \, \overline{N}^G}$ perfect gas eq. of state.

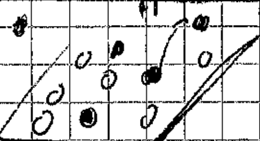
3) $z = \frac{V}{\Lambda_T^3}$ where $\Lambda_T = \left(\frac{2\pi m k_B T}{h^2}\right)^{-1/2}$ in the MB approx.

$$\Xi^{MB} = \exp\left(\frac{V}{\Lambda_T^3} e^{\beta \mu}\right) ; \quad J^{MB} = -\frac{1}{\beta} \frac{V}{\Lambda_T^3} e^{\beta \mu}$$

$$\overline{N}^G = \frac{V}{\Lambda_T^3} e^{\beta \mu} \qquad \overline{E}^G = \frac{3}{2} k_B T \, \overline{N}^G$$

$$p^G_{MB} = \frac{k_B T}{\Lambda_T^3} e^{\beta \mu}$$

8.2) Adsorption of an ideal gas



- Each site can adsorb one atom $\Rightarrow$ energy $-\varepsilon_0$
- System in eq. at Temp T.
- Gaz acts like a reservoir ($N_{gaz} \propto L^3 \gg N_{surf} \propto L^2$)

1) Single site is either empty or occupied

1st natural method
$$\xi_{trap} = \sum_{n=0,1} e^{\beta(\varepsilon_0+\mu)n} = 1 + e^{\beta(\varepsilon_0+\mu)}$$

The sites are independent $\Rightarrow \Xi(T,A,\mu) = \left(1+e^{\beta(\varepsilon_0+\mu)}\right)^A$

2) Other more complicated method:

Calculate the canonical partition function: n particles in A sites.

$$Z = C_A^n \, e^{\beta(n\varepsilon_0)} = Z(T,A,n)$$
$$\Xi = \sum_n e^{n\beta\mu} Z(T,A,n) = \sum_n C_A^n \, e^{\beta(\varepsilon_0+\mu)n} = \left(1+e^{\beta(\varepsilon_0+\mu)}\right)^A$$

$\Rightarrow$ The 1st method is far simpler! $\Rightarrow$ Just focus on single site occupation

3) $$\overline{N} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi = \frac{A}{\beta}\,\beta\,\frac{e^{\beta(\varepsilon_0+\mu)}}{1+e^{\beta(\varepsilon_0+\mu)}} = \frac{A}{1+e^{-\beta(\varepsilon_0+\mu)}}$$

$$\Rightarrow \boxed{\theta = \frac{\overline{N}}{A} = \frac{1}{1+e^{-\beta(\varepsilon_0+\mu)}}}$$ average occupation of a single trap

4) $\mu = -k_B T \ln\frac{Z}{N}$ for a perfect gas described by the M.B approx.

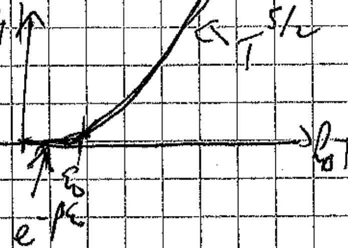
$$= -k_B T \ln\left(\frac{V}{N\Lambda_T^3}\right) \Leftrightarrow e^{\beta\mu} = \frac{N}{V}\Lambda_T^3 = \frac{P}{k_B T}\Lambda_T^3 \quad \text{(perfect gas)}$$

$$\Leftrightarrow e^{\beta\mu} = \frac{P}{\tilde{P}(T)} \quad \text{where } \tilde{P}(T) = k_B T\,\Lambda_T^{-3}$$

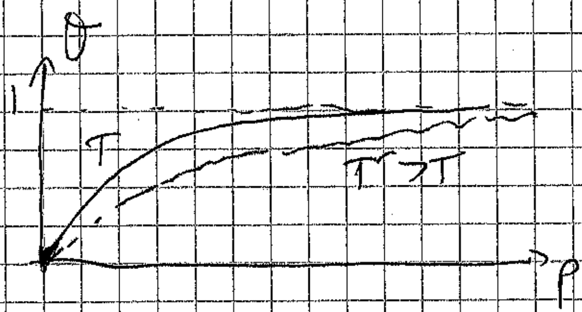
$$\Rightarrow \theta = \frac{1}{1+e^{-\beta\varepsilon_0}\frac{\tilde{P}(T)}{P}} = \frac{1}{1+\frac{P_0(T)}{P}}$$

where $P_0(T) = e^{-\beta\varepsilon_0}\,\tilde{P}(T) = e^{-\beta\varepsilon_0}\,k_B T\,\Lambda_T^{-3} \sim (k_B T)^{+5/2}$

We find $\theta = \dfrac{P}{P + P_0(T)}$ where $P_0(T) \propto e^{-\frac{\varepsilon_0}{k_B T}}\, T^{5/2}$



5)

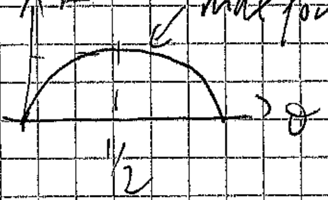


$P_0(T) \nearrow$ with T

Applicat°: The averagage populat° on the surface $\searrow$ when $T \nearrow$ at fixed P

6) $\mathrm{var}(N) = \left(\frac{1}{\beta}\frac{\partial}{\partial\mu}\right)^2 \ln \Xi$

we find $\dfrac{\mathrm{var}(N)}{A} = \dfrac{1}{\beta}\dfrac{\partial}{\partial\mu}\dfrac{\bar{N}}{A} = \theta(1-\theta)$



8.3) Fluctuations of energy

$$\bar{E}^g(T, V, \mu) = \bar{E}^c\left(T, V, \bar{N}^g(T, V, \mu)\right)$$

A) $g(k) \equiv \langle e^{kx} \rangle$

$$g(k) \underset{k\to 0}{\sim} 1 + k\langle x\rangle + \frac{1}{2}k^2\langle x^2\rangle + O(k^3)$$

$$\simeq \exp\left(k\langle x\rangle + \frac{1}{2}k^2\langle x^2\rangle - \frac{1}{2}k^2\langle x\rangle^2 + O(k^3)\right)$$

Indeed if we expand the $\exp(\;\;)$ we recover $g(k)$

$$\Rightarrow \ln g(k) = k\langle x\rangle + \frac{1}{2}k^2 \underbrace{\left(\langle x^2\rangle - \langle x\rangle^2\right)}_{\mathrm{var}(x)} + O(k^3)$$

Thus $\boxed{\mathrm{var}(x) = \dfrac{d \ln g(k)}{dk^2}\Big|_{k=0}}$

B) $P_\ell^c \propto e^{-\beta E_\ell} \to E_\ell \propto -\dfrac{\partial}{\partial\beta} \Rightarrow \mathrm{var}(E_\ell) = \left(-\dfrac{\partial}{\partial\beta}\right)^2 \ln Z = -\dfrac{\partial \bar{E}^c}{\partial\beta}$

$$\boxed{\mathrm{var}(E_\ell) = -\frac{\partial T}{\partial\beta}\frac{\partial \bar{E}^c}{\partial T} = k_B T^2 C_V}$$

fluctuat° $\to$ … $\to$ response

c) We want to prove $\mathrm{var}_g(E) = \mathrm{var}_c(E) + \left(\frac{\partial \bar{E}^c}{\partial N}\right)^2 \mathrm{var}_g(N)$

1) In short $E = e \cdot N$
e ← energy per particle.

If N const, $\mathrm{var}_c(E) = N^2\, \mathrm{var}_c(e)$

If N fluctuates, $\mathrm{var}_c(E) = \bar{N}^2\, \mathrm{var}(e) + \bar{e}^2\, \mathrm{var}(N)$

$\bar{e} \to \left(\frac{\partial \bar{E}}{\partial N}\right)^2$ ⇒ makes sense.

2) $P_\ell^G \propto e^{-\beta(E_\ell - \mu N_\ell)}$

This implies $N_\ell \leftrightarrow \frac{1}{\beta}\frac{\partial}{\partial \mu}$ and $E_\ell - \mu N_\ell \leftrightarrow -\frac{\partial}{\partial \beta}$

Therefore $E_\ell \to -\frac{\partial}{\partial \beta} + \frac{\mu}{\beta}\frac{\partial}{\partial \mu}$

Thus $\bar{E}^g = \left(-\frac{\partial}{\partial \beta} + \frac{\mu}{\beta}\frac{\partial}{\partial \mu}\right) \ln \mathcal{Z}$

$\to \mathrm{var}(\bar{E}^g) = \left(-\frac{\partial}{\partial \beta} + \frac{\mu}{\beta}\frac{\partial}{\partial \mu}\right)^2 \ln \mathcal{Z} = \left(-\frac{\partial}{\partial \beta} + \frac{\mu}{\beta}\frac{\partial}{\partial \mu}\right) \bar{E}^g$

3) We need to relate $\frac{\partial \bar{E}^g}{\partial T}$ and $\frac{\partial \bar{E}^g}{\partial \mu}$ to partial derivatives of $\bar{E}^c$

$$\bar{E}^g(T,V,\mu) = \bar{E}^c(T,V,\bar{N}^g(T,V,\mu))$$

$$\begin{cases} \dfrac{\partial \bar{E}^g}{\partial T} = \dfrac{\partial \bar{E}^c}{\partial T} + \dfrac{\partial \bar{E}^c}{\partial N}\cdot\dfrac{\partial \bar{N}^g}{\partial T} \\[2ex] \dfrac{\partial \bar{E}^g}{\partial \mu} = \dfrac{\partial \bar{E}^c}{\partial N}\cdot\dfrac{\partial \bar{N}^g}{\partial \mu} \end{cases}$$

$$\Rightarrow \mathrm{var}(\bar{E}^g) = \underbrace{k_B T^2 \frac{\partial \bar{E}^c}{\partial T}}_{\mathrm{var}_c(E)} + \underbrace{k_B T^2\left(\frac{\partial \bar{E}^c}{\partial N}\frac{\partial \bar{N}^g}{\partial T} + \frac{\mu}{T}\frac{\partial \bar{E}^c}{\partial N}\cdot\frac{\partial \bar{N}^g}{\partial \mu}\right)}_{k_B T \frac{\partial \bar{E}^c}{\partial N}\left(T\frac{\partial \bar{N}^g}{\partial T} + \mu\frac{\partial \bar{N}^g}{\partial \mu}\right)} \quad (*)$$

4) Thermodynamic identity:

$$T\left(\frac{\partial N}{\partial T}\right)_{\mu,V} + \mu\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \left(\frac{\partial E}{\partial \mu}\right)_{T,V} = \left(\frac{\partial E}{\partial N}\right)_{T,V}\left(\frac{\partial \bar{N}^g}{\partial \mu}\right)_{T,V}$$

Proof: We start from $dE = T\,dS - p\,dV + \mu\,dN$

We divide by $d\mu$ at V, T const

$$\left(\frac{\partial E}{\partial \mu}\right)_{T,V} = T\left(\frac{\partial S}{\partial \mu}\right)_{T,V} + \mu\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$$

However $G = E - TS - \mu N$

$$dG = -S\,dT - p\,dV - N\,d\mu \quad \text{(Maxwell identity)}$$

Therefore $\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = \left(\frac{\partial N}{\partial T}\right)_{\mu,V}$

$$\Rightarrow T\frac{\partial \bar{N}^g}{\partial T} + \mu\frac{\partial \bar{N}^g}{\partial \mu} = \frac{\partial \bar{E}^g}{\partial \mu} = \frac{\partial \bar{E}^c}{\partial N}\frac{\partial \bar{N}^g}{\partial \mu} \quad \checkmark \text{OK}$$

Injecting into (*)

$$\mathrm{var}(\bar{E}^g) = k_B T^2 \frac{\partial \bar{E}^c}{\partial T} + \frac{1}{\beta}\left(\frac{\partial \bar{E}^c}{\partial N}\right)^2 \cdot \left(\frac{\partial \bar{N}^g}{\partial \mu}\right)$$

$$\Rightarrow \mathrm{var}_g(E) = \mathrm{var}_c(E) + \left(\frac{\partial \bar{E}^c}{\partial N}\right)^2 \mathrm{var}_g(N) \quad \checkmark$$

D) Application: Perfect gas

Canonical: $Z^{MB} \propto \frac{1}{N!}\frac{V^N}{\Lambda_T^{3N}} \sim e^N\left(\frac{V}{N}\right)^N \beta^{-\frac{3N}{2}}$

$$\bar{E}^c = \frac{3N}{2}k_B T \quad \& \quad \mathrm{var}_c(E) = \frac{3N}{2}(k_B T)^2$$

Grand canonical

$$\Xi^{MB} = \exp\left(\frac{V}{\Lambda_T^3}e^{\beta\mu}\right)$$

$$\bar{N}^g = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \Xi^{MB} = \frac{V}{\Lambda_T^3}e^{\beta\mu} \quad \& \quad \mathrm{var}_g(N) = \bar{N}^g$$

$$\xrightarrow{\frac{1}{\beta}\frac{\partial}{\partial\mu}}$$

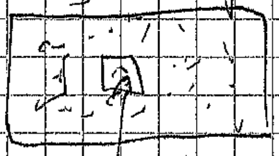
$$\mathrm{var}_g(E) = \frac{3\bar{N}^g}{2}(k_B T)^2 + \left(\frac{3}{2}k_B T\right)^2 \cdot \bar{N}^g$$

$$= \frac{15}{4}\bar{N}^g (k_B T)^2$$

$$\frac{\sqrt{\mathrm{var}(E)}}{\bar{E}} = \begin{cases} 0 & \mu\text{canonical} \\ \sqrt{\frac{2}{3N}} & \text{canonical} \end{cases} \longrightarrow \sqrt{\frac{5}{3N}} \quad \text{grand canonical}$$

8.5) Density fluctuations in a fluid

1) a) Order of magnitude



$P = 1\,\mathrm{atm} = 10^5\,\mathrm{Pa}$
$T = 300\,\mathrm{K}$; $V = 1\,\mathrm{cm}^3 \nearrow N = \frac{PV}{k_B T} \sim 2.5\,10^{19}$

b) $v \approx 500\,\mathrm{m/s}$; $\tau \approx 2\,\mathrm{ns} \rightarrow l = v\tau \approx 1\,\mu\mathrm{m}$ (distance between two collisions)

$$D = \frac{l^2}{3\tau} = \frac{vl}{3} \sim 10^{-4}\,\mathrm{m^2 s^{-1}}$$

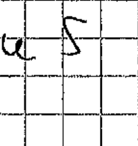
The typical distance traveled $x \sim \sqrt{2Dt}$ (diffusive motion)

For $x = 1\,\mathrm{cm}$ ("size" of the box)

$$t = \frac{x^2}{2D} = \frac{10^{-4}}{2 \cdot 10^{-4}} \sim 0.5\,\mathrm{s}$$

$\Rightarrow$ On average, a molecule remains $0.5\,\mathrm{s}$ inside $V = 1\,\mathrm{cm}^3$

c) Consider a surface S



$\phi = \frac{\delta N_\tau}{\tau} = n v . S$ (n = density)

= nb of particles/unit time.

Therefore during a time τ $\delta N_\tau = n v \tau S$

$= n\, l \times S = n\, l\, L^2$

$$\frac{\delta N_\tau}{N} \simeq \frac{n\, l L^2}{n . L^3} \simeq \frac{l}{L} = \frac{10^{-6}}{10^{-2}} \simeq 10^{-4}$$

d) $\frac{\delta N_\tau}{N} \ll 1$ (10^{-4}) $\Rightarrow$ Therefore particles remain a rather long time inside V before leaving it. They will typically undergo ~~[illegible]~~ $2.5\,10^8$ collisions before leaving L

$\Rightarrow$ Enough to thermalize

Therefore as soon as $\frac{l}{L} \ll 1$, makes sense to consider the gas inside V as in grand-canonical formalism

2) $\bar{N}^g = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln \Xi$; $\Delta N^2 = \mathrm{Var}_g(N) = \left(\frac{1}{\beta}\frac{\partial}{\partial\mu}\right)^2 \ln \Xi = \frac{1}{\beta}\frac{\partial \bar{N}^g}{\partial\mu}$

$$\Delta N^2 = k_B T \frac{\partial \bar{N}^g}{\partial\mu}$$

3) $\mu = f\left(\frac{N}{V}, T\right)$; $p = g\left(\frac{N}{V}, T\right)$

intensive   intensive

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = \frac{1}{V}\frac{\partial f}{\partial n}(n,T) \; ; \left(\frac{\partial\mu}{\partial V}\right)_{T,N} = -\frac{N}{V^2}\frac{\partial f}{\partial n}(n,T) \Rightarrow \left(\frac{\partial\mu}{\partial N}\right)_{T,V} = -\frac{V}{N}\left(\frac{\partial\mu}{\partial V}\right)_{T,N}$$

Similarly $\left(\frac{\partial p}{\partial N}\right)_{T,V} = -\frac{V}{N}\left(\frac{\partial p}{\partial V}\right)_{T,N}$

We have $dF = -SdT - p\,dV + \mu\,dN$

And $\frac{\partial^2 F}{\partial V \partial N} = \frac{\partial^2 F}{\partial N \partial V} \Rightarrow -\left(\frac{\partial p}{\partial N}\right)_{T,V} = \left(\frac{\partial\mu}{\partial V}\right)_{T,N}$

4) $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \Rightarrow$ How the volume changes as we change the pressure.

$$K_T = -\frac{1}{V}\frac{1}{\left(\frac{\partial p}{\partial V}\right)_{T,N}} = -\frac{1}{V}\frac{1}{-\frac{N}{V}\left(\frac{\partial p}{\partial N}\right)_{T,V}} = \frac{-1}{N\left(\frac{\partial\mu}{\partial V}\right)_{T,N}} = \frac{1}{\frac{N^2}{V}\left(\frac{\partial\mu}{\partial N}\right)_{T,V}}$$

Thus $N^2 \frac{K_T}{V} = \left(\frac{\partial N}{\partial\mu}\right)_{T,V} \equiv \frac{\partial \bar{N}^g}{\partial\mu} = \frac{\Delta N^2}{k_B T}$

$$\Rightarrow \boxed{\underbrace{\frac{\Delta N^2}{N}}_{\text{fluctuat}^o} = n k_B T \underbrace{K_T}_{\text{response}}}$$

Another example of fluctuat° dissipat° relations

5) Classical ideal gas

$$pV = N k_B T \Rightarrow K_T^{GP} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{V}\left(\frac{-N k_B T}{p^2}\right) = \frac{1}{p}$$

$$K_T^{GP} = \frac{1}{p} = \frac{1}{n k_B T} \Rightarrow \boxed{\frac{\Delta N^2}{N} = \frac{K_T}{K_T^{GP}}}$$

6) $n(\vec r) = \sum_{i=1}^{N} \delta(\vec r - \vec r_i)$ local density in $\vec r$

$\hookrightarrow N = \int n(\vec r)\,d\vec r$ (def)

$$\mathrm{var}(N) = \overline{\left(\int d\vec r\, n(\vec r)\right)^2} - \left(\overline{\int d\vec r\, n(\vec r)}\right)^2$$

$$\mathrm{var}(N) = \int d\vec{r}\, d\vec{r}\,' \Big[\overline{n(\vec{r})\, n(\vec{r}\,')} - \underbrace{\overline{n(\vec{r})}\ \overline{n(\vec{r}\,')}}_{n^2} \Big]$$

Homogeneous fluid $\overline{n(\vec{r})n(\vec{r}\,')} = n\,\delta(\vec{r}-\vec{r}\,') + n^2 g(\vec{r}-\vec{r}\,')$ ↑ pair correlat° funct°

$g(\vec{r}-\vec{r}\,')$ = proba that 2 particles be separated by $\vec{r}-\vec{r}\,'$

b) if $\|\vec{r}-\vec{r}\,'\| \to \infty$ then $\overline{n(\vec{r})n(\vec{r}\,')} \simeq n^2$ ↑ uncorrelated. $\Big\} \Rightarrow g(\vec{r}) \xrightarrow[\|\vec{r}\| \to \infty]{} 1$

c) $\mathrm{var}(N) = \int d\vec{r}\, d\vec{r}\,' \left[n\,\delta(\vec{r}-\vec{r}\,') + n^2 g(\vec{r}-\vec{r}\,') - n^2 \right]$

$$= nV + n^2 V \int d\vec{r}\,\left(g(\vec{r}) - 1 \right)$$

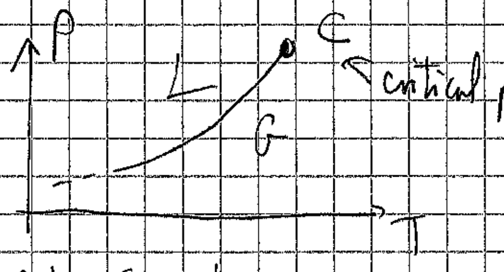
$$= N \left[1 + n \int d\vec{r}\,\left(g(\vec{r}) - 1 \right) \right]$$

isotropic

$$= N \left[1 + n \int_0^{+\infty} 4\pi r^2\, dr \left(g(r) - 1 \right) \right]$$

$$= N\, n k_B T\, \kappa_T$$

Therefore $\underbrace{n k_B T\, \kappa_T}_{\text{thermo}} = 1 + n \int_0^{+\infty} \underbrace{4\pi r^2 dr \left(g(r) - 1 \right)}_{\text{microscopic distribut°}}$



At C, $\kappa_T \to \infty \Rightarrow \int dr\, r^2 \left(g(r) - 1 \right) \to \infty$

This implies long wave length correlat°

Modèle d'Ising et gaz sur réseau

Ising $\quad H_{Ising} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \underbrace{B}_{\text{champ magnétique}} \sum_i \sigma_i$

$J > 0$: interaction ferro.

Compétition :
* interaction (alignement des spins)
* champ magnétique (alignement sur B)
* agitation thermique.

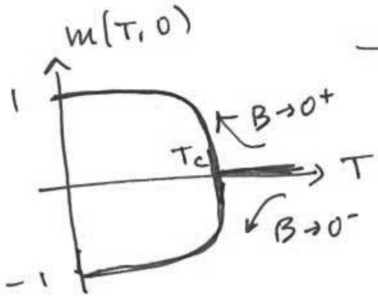
ex: 1D : easy to solve. No phase transition

2D : difficult to solve. T_c given by $\operatorname{sh} \frac{2J}{T_c} = 1$ at $B=0$ — Onsager 1941

$$\frac{C(T, \overset{B}{0})}{k_B} \simeq \frac{2}{\pi} \left(\frac{2J}{T_c}\right)^2 \left(-\ln\left|1 - \frac{T}{T_c}\right| + \text{cste}\right)$$

$$m(T,0) = \begin{cases} 0 & \text{for } T > T_c \\ \left[1 - (\operatorname{sh} 2\beta J)^{-4}\right]^{1/8} & \text{for } T < T_c \end{cases}$$

C.N. Yang. Phys. Rev <u>85</u> 809 (1952)

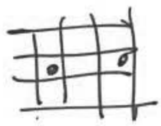


$$m(T,0) = \lim_{B \to 0^\pm} \overbrace{\lim_{N \to \infty}}^{\text{thermo limit}} \underbrace{\frac{1}{N} \frac{-\partial F_{Ising}(T,B,N)}{\partial B}}$$

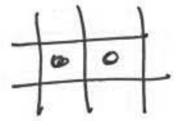
$f(T,B) = \lim_{N \to \infty} \frac{F_{Ising}}{N}$ is non analytic

$$f(T,B) = \text{cste} - m \times |B| + O(B^2)$$
for $T < T_c$

Gaz sur réseau.

$\rightarrow$ 

n_i = occupation of site i

* hard core repulsion
  $\Rightarrow n_i = 0$ or 1
* attraction (van der Waals)  $\Rightarrow$ energy -4ε

$$H_{LG} = -4\varepsilon \sum_{\langle ij \rangle} n_i n_j \quad \text{with } \mathcal{N} = \sum_i n_i$$

Dans l'ens. grand canonique :

$$\Xi_{LG} = \sum_{\{n_i\}} e^{-\beta(H_{LG} - \mu \mathcal{N})}$$

→ no more constraint on $\sum_i n_i$

$$\tilde{H}_{LG} = H_{LG} - \mu \mathcal{N} = -\varepsilon \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i$$

write $n_i = \frac{\sigma_i + 1}{2}$ $\quad \sigma_i \in \{-1, +1\} \to n_i \in \{0, 1\}$

$$\tilde{H}_{LG} = -\varepsilon \underbrace{\sum_{\langle ij \rangle} (\sigma_i + 1)(\sigma_j + 1)} - \frac{\mu}{2} \sum_i (\sigma_i + 1)$$

$$\underbrace{\sum_{\langle ij \rangle}}_{\Sigma \text{ bonds}} = \frac{1}{2} \underbrace{\sum_i}_{\Sigma \text{ sites}} \sum_{j \in v(i)}$$

$$\sum_{\langle ij \rangle} \sigma_i \sigma_j + 2 \underbrace{\sum_{\langle ij \rangle} \sigma_i}_{q \sum_i \sigma_i} + \underbrace{\sum_{\langle ij \rangle} 1}_{\frac{qN}{2}}$$

q = # of neighbours (coordination nb)

$$\tilde{H}_{LG} = -\varepsilon \sum_{\langle ij \rangle} \sigma_i \sigma_j - q\varepsilon \sum_i \sigma_i - \frac{qN}{2}\varepsilon - \frac{\mu}{2} \sum_i \sigma_i - \frac{\mu N}{2}$$

$$\boxed{\tilde{H}_{LG} = \underbrace{-\varepsilon \sum_{\langle ij \rangle} \sigma_i \sigma_j - \left(q\varepsilon + \frac{\mu}{2}\right) \sum_i \sigma_i}_{H_{Ising}} - \frac{N}{2}(q\varepsilon + \mu)}$$

mapping:

Ising	Lattice gas
σ_i	$n_i = \frac{\sigma_i + 1}{2}$
J	ε
B	$q\varepsilon + \frac{\mu}{2}$
H_{Ising}	$\tilde{H}_{LG} + \frac{N}{2}(q\varepsilon + \mu)$

$$\Rightarrow Z_{Ising} = \Xi_{LG} \times e^{-\beta \frac{N}{2}(q\varepsilon+\mu)}$$

$$\boxed{F_{Ising} = J_{LG} + \frac{N}{2}(q\varepsilon+\mu)}$$

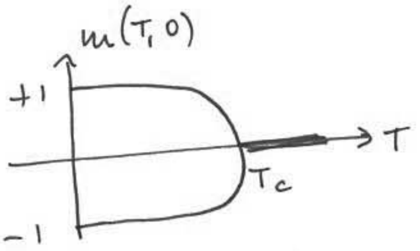
free energy — grand potential

<u>check:</u> $\frac{\partial}{\partial B} = 2\frac{\partial}{\partial \mu}$

$$\overline{n_i} = \frac{\overline{N}}{N} = \frac{-1}{N}\frac{\partial}{\partial\mu}\underbrace{J_{LG}}_{F_{Ising}-\frac{N}{2}(q\varepsilon+\mu)} = \frac{1}{N}\Big(\overbrace{-\frac{1}{2}\frac{\partial}{\partial B}F_{Ising}}^{+\frac{m}{2}} + \frac{N}{2}\Big) = \frac{m+1}{2}$$

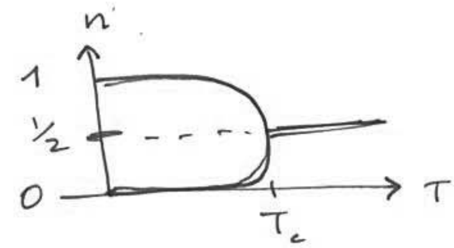
OK $\overline{n_i} = \frac{\overline{\sigma_i}+1}{2}$

<u>Ising:</u>



for $B = 0$

$\longrightarrow$ <u>Lattice gas</u>



for $\boxed{\mu = -2q\varepsilon}$

below T_c: two possible phases: high or low density
$\Rightarrow$ gas and liquid.