note

$\Omega = \frac{1}{N!}\sigma(E,V,N)$

σ_0 → importante en quantum mech.

↓

cada microestado ← incerteza ocupa al menos un volumen de $\Delta p \Delta q \gtrsim h$

↓

$\Delta^{3N}p\, \Delta^{3N}q \gtrsim h^{3N}$

$S = 0$ → microestado definido $(\Omega = 1)$

↓

cristales ideales a $T=0$.

tercera ley de la termodinámica

Para gases idénticos, el proceso debe ser reversible

→ $\Delta S = 0$

↓

$N!$ formas de enumerar una partícula

· caso de objetos distinguibles (átomos localizados en una grilla), el factor de *Gibbs* no se debe agregar.

$$\Sigma(E,V,N) = \sum_{E' \le E} \Omega(E',V,N)$$

· Σ → mean function

$$g(E,V,N) = \frac{\partial}{\partial E}\Sigma(E,V,N)$$

→ mean density of states. (mean # of states per energy interval)

g: density of states, mean # of states per energy interval ΔE.

Σ: # of all microstates of a quantum system having an energy lower than E.

$\propto$ volume of the positive octant $(n_i > 0)$ con $E =$ cte.

· vol. 3N-D octant of a sphere with radius $\sqrt{E^*} = (8mEL^2/h^2)^{1/2}$

↳ 2^{3N} octants and with $L^2 = V^{2/3}$.

$$S = NK\left[\frac{5}{2} + \ln\left\{\frac{V}{Nh^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right\}\right]$$

Sackur-Tetrode equation.

→ Gibbs correction:

$S = k \ln \Omega$ → indistinguishable objects:

$\Omega(E,V,N) = g(E,V,N)E$ → Dimensionless # of states.

$g(E) = \frac{\partial \Sigma(E)}{\partial E}$ → número de estados x intervalo de energía: g.

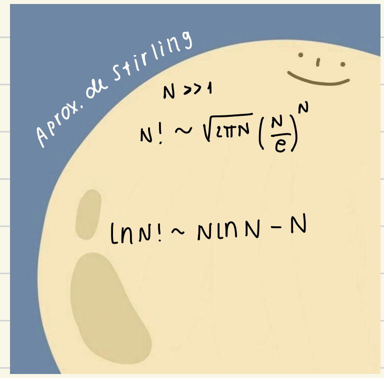
$$\Sigma(E) = \frac{1}{N!\,h^{3N}} \int_{H(q_\nu,p_\nu)\le E} d^{3N}p\, d^{3N}q$$

Note Pad

· Division by h^{3N} → # of quantum mechanical states within this volume.

* cte σ se mantiene en el límite clásico.

Resumen Mesta



Prob. de obtener el resultado r:

$P_r = \lim_{N\to\infty} \frac{N_r}{N}$; N: n° de veces que se repite el exp.

· Distrib. binomial : N° de éxitos en un n° fijo de ensayos

$P_N(r) = \binom{N}{r} p^r (1-p)^{N-r}$ $\longrightarrow$ Prob. de obtener éxito r veces.

$\binom{N}{r} = \frac{N!}{(N-r)!\, r!}$

Promedio: $\mu_N = \bar{r} = \langle r \rangle = \sum_{r=0}^{N} r P_r = pN$

Varianza: $\sigma_N^2 = \sum_{r=0}^{N} (r-\mu_N)^2 P_N(r) = Np(\underbrace{1-p}_{q})$

Desviación estándar: $\sigma_N = \sqrt{Npq}$; $\frac{\sigma_N}{N} \xrightarrow[N\to\infty]{} 0$

· Distrib. Poisson: N° de eventos que ocurren en un intervalo de espacio o tiempo.

$P_N(r) = \binom{N}{r} p^r (1-p)^{N-r}$ $\left.\begin{matrix} N >> 1 \\ p << 1 \end{matrix}\right\}$ $pN = \mu$ finito. ; $e^x = \lim_{N\to\infty}\left(1 + \frac{x}{N}\right)^N$

$= \frac{(Np)^r}{r!} \underbrace{\left(1 - \frac{Np}{N}\right)^N}_{e^{-\mu}} \underbrace{(1-p)^{-r}}_{\approx 1} \underbrace{\frac{N!}{(N-r)!} \frac{1}{N^r}}_{\approx 1}$

$\boxed{P_N(r) = \frac{\mu^r}{r!} e^{-\mu}}$

· Distrib. normal : Datos continuos y simétricos

$P_N(r) = \binom{N}{r} p^r (1-p)^{N-r}$

$N >> 1$

$r \sim NP = \mu$ → r cerca del promedio

$\delta = r - NP$ → $\frac{\delta}{N} << 1$

$= \frac{1}{\sqrt{2\pi}} \sqrt{\frac{N}{(N-r)r}} \left(\frac{Np}{r}\right)^r \left(\frac{N(1-p)}{N-r}\right)^{N-r}$ / ln()

$P_N(r) = \frac{1}{\sqrt{2\pi N pq}} e^{-(r-Np)^2/2Npq}$

$\boxed{P_N(r) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(r-\bar{r})^2/2\sigma^2}}$

Postulado sist. aislado en equilibrio

· Todos los microestados (Ω) compatibles con un macroestado dado son igualmente probables.

↳ Equilibrio : las cantidades promedio del sistema no cambian en el tiempo.

Entropía: N° de microestados accesibles

$S = k_b \ln \Omega$

↳ $\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T}$, $\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}$, $\frac{\partial S}{\partial N} = -\frac{\mu}{T}$, $\underbrace{C}_{\text{capacidad calórica.}} = T\frac{\partial S}{\partial T}$

$$\Omega(E,V,N) = \int_{\vec{r}\in V} \frac{d^{3N}p\, d^{3N}r}{h^{3N}} = \frac{V^N}{h^{3N}} \underbrace{\int_{\sum \vec{p}_i^{\,2} = 2mE} d^{3N}p}_{S_{3N}(\sqrt{2mE})} = \frac{V^N}{h^{3N}} (3N) \left(\frac{2\pi e}{3N}\right)^{3N/2} (2mE)^{3N/2}$$

Dem Esfera de radio r en n dim.

- Volumen: $V_n(r) = \alpha_n r^n$
- Superficie: $S_n(r) = n\alpha_n r^{n-1}$

Se tiene $I_n = \int_{-\infty}^{\infty} dx_1 \dots dx_n\, e^{-(x_1^2 + \dots + x_n^2)} = \sqrt{\pi}^{\,n}$

$$\int_0^\infty S_n(r)\, dr\, e^{-r^2} = \sqrt{\pi}^{\,n}$$

$$\alpha_n n \int_0^\infty r^{n-1} dr\, e^{-r^2} = \sqrt{\pi}^{\,n}$$

$$\frac{\alpha_n n}{2} \underbrace{\int_0^\infty du\, u^{\frac{n}{2}-1} e^{-u}}_{\Gamma(\frac{n}{2})} = \sqrt{\pi}^{\,n} \quad ; \ \Gamma\left(\tfrac{n}{2}\right) = \left(\tfrac{n}{2}-1\right)!$$

$$\Gamma\left(\tfrac{n}{2}+1\right) = \tfrac{n}{2}\Gamma\left(\tfrac{n}{2}\right)$$

$$\Rightarrow \alpha_n = \pi^{n/2} / \Gamma(n/2+1) \overset{\text{stirling}}{=} \left(\frac{2\pi e}{n}\right)^{n/2} \frac{1}{\sqrt{\pi n}} \quad ; \ n \gg 1$$

Fórmula de Sackur-Tetrode.

$$\boxed{S = k_B \ln\left(\frac{\Omega}{N!}\right) = N k_B \left[\ln \frac{V}{N} + \frac{3}{2}\ln\left(\frac{E}{N} \cdot \frac{4\pi m e}{3h^2}\right)\right]}$$

; $N!$ → Paradoja de Gibbs. (para part. indistinguibles) → viene de que S debe ser extensiva ($2N \to 2S$)

$$\Omega_{indist} = \frac{\Omega}{N!}$$

- $\frac{\partial S}{\partial E} \to E = \frac{3}{2} N k_b T$
- $\frac{\partial S}{\partial V} \to PV = k_b T N$
- $\left.\frac{\partial S}{\partial T}\right|_P \to C_p = \frac{5}{2} N k_b$ → se agrega un trabajo mecánico.
- $\left.\frac{\partial S}{\partial T}\right|_V \to C_v = \frac{3}{2} N k_b$

Prop.

1) $dS = \left.\frac{\partial S}{\partial E}\right|_{V,N} dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \left.\frac{\partial S}{\partial N}\right|_{E,V} dN$

$dS = \frac{1}{T} dE + \frac{P}{T} dV + \frac{-\mu}{T} dN \to dE = TdS - PdV + \mu dN$

2) $TS = E + PV - \mu N$

Ej: 2 sist. aislados:

$\Omega_T = \Omega_1(E_1, V_1, N_1)\, \Omega_2(E_2, V_2, N_2)$.

$S(E,V,N) = S_1(\bar{E}_1, \bar{V}_1, \bar{N}_1) + S_2(E - \bar{E}_1, V - \bar{V}_1, N - \bar{N}_1)$

El nuevo estado de equilibrio está caracterizado por un máximo de la entropía

Ensamble canónico

· Hay intercambio de energía

· función partición canónica: $Q = \sum_s e^{-\beta E_s}$; $\beta = \frac{1}{k_b T}$

· Energía interna: $\bar{E} = -\frac{\partial}{\partial\beta} \ln Q$

· Energía libre de Helmholtz: $F = -T k_b \ln Q = \bar{E} - TS$

· $P = -\frac{\partial F}{\partial V}\Big|_T = k_b T \frac{\partial}{\partial V} \ln Q$

· Energía libre de Gibbs: $G = \bar{E} - TS + PV$

$= F + PV$

$= -k_b T \ln Q + V k_b T \frac{\partial}{\partial V} \ln Q \Big|_T$

· $C_v = \frac{\partial \langle E \rangle}{\partial T}\Big|_V$, $C_p = \frac{\partial \langle E \rangle}{\partial T}\Big|_P$

Ej Gas ideal N part. idénticas:

$$Q = \frac{V^N}{h^{3N}} \frac{1}{N!} \int d^{3N}p \, e^{-\beta \sum \frac{\vec{p}_i^{\,2}}{2m}}$$

$$= \frac{V^N}{h^{3N} N!} \sqrt{\pi 2 m k_b T}^{\,3N}$$

$$\bar{E} = \frac{3}{2} N k_b T$$

N obj. idénticos que no interactúan

$$Q = \left(\sum_{S_1} e^{-\beta E_{S_1}}\right) \dots \left(\sum_{S_N} e^{-\beta E_{S_N}}\right) = (Q_1)^N$$

Ensamble Gran canónico

· Intercambio de E y N.

· Func. gran partición: $\mathcal{Q} = \sum_{N=0}^{\infty} \sum_{E} \Omega(E, N)\, e^{-\beta(E - \mu N)} \longrightarrow \mathcal{Q} \approx e^{-k_b^{-1} S - \beta\langle E \rangle + \beta\mu\langle N \rangle}$

energía (bajo $\sum_E$)

N° de estados c/ energía E $= e^{S/k}$

· Gran Potencial $\Phi = -k_b T \ln \mathcal{Q}$

$\Phi = -PV = -TS + \langle E \rangle - \mu \langle N \rangle$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Q}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Q} + \mu \langle N \rangle$$

Recordar:

* Entropía se maximiza sólo cuando el sist. está aislado.

Adsorción

· A sistemas, c/u con dos estados : 0 partículas, energía 0
1 partícula, energía $-\varepsilon_0$

· $\mathcal{Q} = \left(1 + e^{\beta(\varepsilon_0 + \mu)}\right)^A$

$$\boxed{\langle N \rangle = \frac{A}{\beta} \frac{\partial}{\partial \mu} \ln\left(1 + e^{\beta(\varepsilon_0 + \mu)}\right)} \longrightarrow \text{"Tasa de adsorción"} \quad \boxed{\frac{\langle N \rangle}{A} = \frac{1}{1 + e^{-\beta(\varepsilon_0 + \mu)}}}$$

n° promedio de part. absorbidas.

$$\boxed{\langle E \rangle = -\varepsilon_0 \langle N \rangle}$$

Reacciones químicas en equilibrio

Relaø de Gibbs-Duhem:

$E = TS - PV + \sum_i \mu_i N_i$, $0 = SdT - VdP + Nd\mu$

si me las arreglo $T = cte$, $P = cte$ $\longrightarrow$ en equilibrio $dG = \boxed{0 = \sum \mu_i \nu_i}$ ↳ coef. estequiométrico.

$dG = \sum_i \mu_i \, dN_i \longrightarrow dN_i \propto \nu_i$

· Si $\boxed{\mu_i = \left.\frac{\partial F_i}{\partial N_i}\right|_{T,V}}$ y $\boxed{F_i = -k_bT \ln Q_i}$; $Q = (q_i)^{N_i}/N_i!$

$= -k_bT[N_i \ln q_i - \ln N_i!]$

$\approx -k_bT[N_i \ln q_i - N \ln N_i + N_i]$

$\rightarrow \mu_i = -k_bT\left[\ln q_i - \cancel{\frac{N}{N}} - \ln N_i + \cancel{1}\right]$

$$\boxed{\mu_i = -k_bT \cdot \ln(q_i/N_i)}$$

ley de acción de masas

$$\prod_i \left(\frac{q_i}{V}\right)^{\nu_i} = \prod_i \Big(\underbrace{\frac{N_i}{V}}_{\text{concentraø del i-ésimo reactivo.}}\Big)^{\nu_i} = K_c$$

· Energía de ligazón de una part. compuesta:

$\varepsilon_{Tot} = \varepsilon_{Tras} + \varepsilon_{vib} + \varepsilon_{rot} - \varepsilon$

$Q = Q_0 e^{\beta \varepsilon N}$

$\rightarrow \ln Q = \ln Q_0 + \beta \varepsilon N \longrightarrow F = F_0 - N\varepsilon$

Estados de un sist. cuántico.

Ej Partícula de masa m en una caja 1D de ancho a.

$\rightarrow \hat{H}\psi = \varepsilon\psi$, $\hat{H} \rightarrow \frac{\hbar k^2}{2m}$

$\rightarrow$ Si $\psi(x) = A_n e^{ik_nx} \longrightarrow$ C.B: $A_n e^0 = A_n e^{ik_na}$

$1 = e^{ik_na}$

$\boxed{k_n a = n\pi}$

· $\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$

Para 1 partícula:

· $z_1 = \sum_{n=0}^{\infty} e^{-\beta\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2} = \sum_{n=0}^{\infty} e^{-\beta\frac{\hbar^2}{2m}\frac{\pi^2}{a^2}\cdot n^2} \longrightarrow \int_0^\infty dn \, e^{-\frac{\beta\hbar^2\pi^2}{2ma^2}n^2} \longrightarrow$ Gaussiana $\longrightarrow = \int_0^\infty \underbrace{\frac{dE}{\sqrt{E}}\sqrt{\frac{2ma^2}{\hbar^2\pi^2}}}_{\rho(E) \rightarrow \text{densidad de estados.}} e^{-\beta E}$

$= \frac{1}{2}\sqrt{\frac{\pi}{\beta\hbar^2\pi^2/2ma^2}}$

$= \frac{1}{2}\frac{1}{\pi}\sqrt{\frac{2ma^2\pi}{\beta\hbar^2}}$

$\rightarrow z = z_1^N$

$\rightarrow U = \frac{N}{2}k_bT$

$F = -k_bT \ln z$

$P = -\frac{\partial F}{\partial a}$ } Fuerza!

$\boxed{\text{Bose - Einstein}}$

$q = \ln \mathcal{Q} = -\sum_k \ln(1 - z e^{-\beta\varepsilon_k}) \longrightarrow -\int_0^\infty d\varepsilon\, g(\varepsilon) \ln(1 - z e^{-\beta\varepsilon})$; Fugacidad : $z = e^{\beta\mu}$

$N = \sum_k \langle n_k \rangle^{BE} = \sum_k \frac{1}{z^{-1} e^{\beta\varepsilon} - 1} \longrightarrow \int_0^\infty d\varepsilon\, g(\varepsilon) \frac{1}{z^{-1} e^{\beta\varepsilon} - 1} = \frac{2\pi V}{h^3}(2m)^{3/2} \frac{2}{3}\beta \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1} e^{\beta\varepsilon} - 1} + \underbrace{\frac{z}{1-z}}_{N_0 \ (\varepsilon = 0)}$

suma de estados : $\sum_k = \int \frac{d^3r\, d^3p}{h^3} = \frac{4\pi V}{h^3} \int p^2 dp = \frac{2\pi V}{h^3} (2m)^{3/2} \int \varepsilon^{1/2} d\varepsilon$

Densidad de estados: $g(\varepsilon) = \frac{d\Sigma}{d\varepsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2}$

Sol. $g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}\, dx}{z^{-1} e^x - 1} = \sum_{k=1}^\infty \frac{z^k}{k^n}$, $0 \leq z \leq 1$

$\hookrightarrow g_n(1) = \zeta(n)$, $n > 1$

· Fotones : Ultrarelativistic Bose-Gas :

$\varepsilon_k = c|\vec{p}| = \hbar c |k|$

· $\sum = \int \frac{d^3r\, d^3p}{h^3} = \frac{4\pi V}{h^3} \int_0^\infty p^2 dp = \frac{4\pi V}{h^3 c^3} \int_0^\infty \varepsilon^2 d\varepsilon$

· $g(\varepsilon) = \frac{d\Sigma}{d\varepsilon} = \frac{4\pi V}{h^3 c^3} \varepsilon^2 \cdot g$

$\hookrightarrow$ spin

· $\mu = 0$: It cost no energy to add arbitrarily many particles in the state $\varepsilon = 0$

$\hookrightarrow$ N no se conserva.

$q = -\frac{4\pi V}{(hc)^3} \frac{\beta}{3} \int_0^\infty d\varepsilon \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1}$

· Fonones : Fotones c/ $c = c_s$ = vel. del sonido. , $\varepsilon = \hbar\omega$

ω_D : frecuencia de Debye.

$\frac{V}{2\pi^2} \underbrace{\frac{1}{c_L^3}}_{\text{1 pol. long}} \int_0^{\omega_D} \omega^2 d\omega + \frac{V}{2\pi^2} \underbrace{\frac{2}{c_T^3}}_{\text{2 pol. transv.}} \int_0^{\omega_D} \omega^2 d\omega \Longrightarrow \frac{V}{2\pi^3} \frac{\omega_D^3}{3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) = \underbrace{3N}_{\text{estados}}$

· $U = \frac{\cancel{V}}{\cancel{2\pi}} \int_0^{\omega_D} \underbrace{\left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right)}_{\frac{9\ \cancel{18\pi^2}\ N}{\omega_D^3\ \cancel{V}}} \frac{\omega^2}{e^{\beta\hbar\omega} - 1} d\omega = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \left(\frac{\omega^2}{e^{\beta\hbar\omega} - 1} \cdot \hbar\omega + \frac{\hbar\omega^3}{2} \right) d\omega$

· $C = 3Nk_b\, D(x_0)$

$\hookrightarrow$ Debye function $D(x_0) = \frac{3}{x_0^2} \int_0^{x_0} \frac{x^4 e^x}{e^x - 1} dx \longrightarrow \Theta = \frac{\hbar\omega_c}{k}$ = Temperatura de Debye.

$\rightarrow x_0 \ll 1$: Altas T ($T \gg \Theta$)

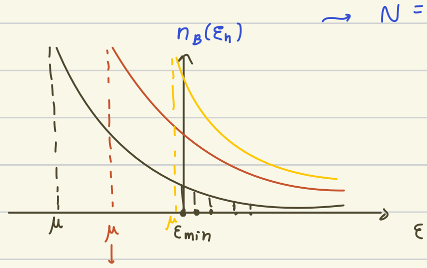
$D(x_0) \rightarrow 1 \implies C_v = 3Nk_b$: equipartición de la energía.

$\rightarrow x_0 >> 1$: ($T \ll \Theta$)

$D(x_0) \rightarrow \frac{3}{x_0^2} \cdot \frac{4\pi^2}{15} \implies C_v = \frac{12\pi^4}{5} N k_b \left(\frac{T}{\Theta}\right)^3$

· condensados de Bose-Einstein

$\rightarrow N = \sum_{\varepsilon_n} n_B(\varepsilon_n)$



si μ crece $\rightarrow$ el nº de ocupac crece para todas las ε.

· Si $\mu \rightarrow \varepsilon_{min}$ se forma el condensado.

(general# $\mu \rightarrow 0$)

En 3D $\left\{ \frac{N}{V} = \frac{1}{2\pi^2} \frac{\sqrt{2m^3}}{\hbar^2} \beta^{-3/2} \underbrace{\int_0^\infty \frac{\sqrt{\varepsilon}\, d\varepsilon}{e^{\varepsilon} - 1}}_{<\infty} + \frac{N_0}{V} \right.$: no caben + part.

En 2D $\frac{N}{V}$ no converge $\rightarrow$ no hay condensado.

Fermi-Dirac

autoestados de energía muy cerca.

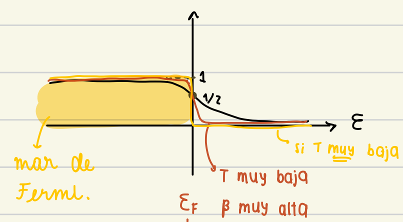
$q = \ln \mathcal{Z} = \sum_k \ln(1 + z e^{-\beta \varepsilon_k}) \longrightarrow \int_0^\infty d\varepsilon\, g(\varepsilon) \ln(1 + z e^{-\beta\varepsilon}) \quad \rightarrow z = e^{\beta\mu}$

$\mathcal{Z}$: Func gran partición

$N = \sum_k \langle n_k \rangle^{FD} = \sum_k \frac{1}{z^{-1} e^{\beta \varepsilon_k} + 1} \longrightarrow \int_0^\infty d\varepsilon\, \boxed{g(\varepsilon)} \frac{1}{z^{-1} e^{\beta\varepsilon} + 1}$

$\rightarrow g(\varepsilon) = \boxed{g} \frac{2\pi V}{h^3} (2m)^{3/2} e^{1/2}$

g: $2s+1$ spin orientations.



· μ debe ser >0!

z en función de $N/V = n$: $z = a_0 + a_1 \left(\frac{N}{V}\right) + a_2 \left(\frac{N}{V}\right)^2 + \ldots$

$$\frac{N_{FD,BE}}{V} = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{z e^{-\beta\varepsilon} \varepsilon^{1/2} d\varepsilon}{1 \pm z e^{-\beta\varepsilon}} = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \varepsilon^{1/2} \underbrace{z e^{-\beta\varepsilon} \sum_{k=0}^\infty (\mp z e^{-\beta\varepsilon})^k}_{\sum_{k=1}^\infty (\mp 1)^{k-1} z^k e^{-k\beta\varepsilon}} d\varepsilon \; ; \quad \sum_k (x)^k = \frac{1}{1-x}, \text{ si } z<1$$

$$= 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \sum_{k=1}^\infty (\mp 1)^{k-1} z^k \underbrace{\int_0^\infty e^{-k\beta\varepsilon} \varepsilon^{1/2} \left(\frac{k\beta}{k\beta}\right)^{1/2} \cdot \frac{d\varepsilon}{k\beta}}_{\left(\frac{1}{k\beta}\right)^{1/2} \Gamma(3/2)}$$

$\Gamma(3/2) = \sqrt{\pi}/2$

En FD

$$\frac{N_{FD,BE}}{V} = g \frac{1}{\lambda^3} \sum_{k=1}^\infty (\mp 1)^{k-1} \frac{z^k}{k^{3/2}} \implies z = \frac{N}{V}\Lambda^3 + \frac{1}{2^{3/2}} \left(\frac{N}{V}\Lambda^3\right)^2 + \ldots$$

g: deg. spin.

$$\frac{P_{FD,BE}}{V} = -\frac{1}{\lambda^3}\sum_{k=1}^{\infty}(\mp 1)^{k-1}\frac{z^k}{k^{5/2}}$$

Término a término,

$$\left.\begin{aligned} a_0 &= 0 \\ a_1 &= \lambda^3 \\ a_2 - a_1^2/2^{3/2} &= 0 \end{aligned}\right\} \quad \left.\frac{P}{k_b T}\right|_{\substack{FD \\ BE}} = \frac{N}{V} \pm \underbrace{\frac{\Lambda^3}{2^{5/2}}\left(\frac{N}{V}\right)^2} + \ldots$$

↳ Fermiones se repelen y Bosones se atraen.

Interacciones

Función partición:

$$Q = \frac{1}{N!}\left(\frac{2\pi m k_bT}{h^2}\right)^{3N/2}\cdot\left[\int d^3r\; e^{-U_{eff}(r)/2k_bT}\right]^N$$

$$\approx \frac{1}{N!}\left(\frac{2\pi m k_bT}{h^2}\right)^{3N/2}\left[\underbrace{(V-V_0)}_{\text{vol. excluido x molécula}} e^{-U_0/2k_bT}\right]^N \longrightarrow \text{Mean field theory}$$

$$= \frac{1}{N!}\frac{1}{\lambda^{3N}}\left[(V-bN)\,e^{\frac{aN}{Vk_bT}}\right]^N$$

$$= Q_{ideal}\left[\left(1-\frac{bN}{V}\right)e^{\frac{aN}{Vk_bT}}\right]^N$$

$$V_0 = \frac{V_0^{TOT}}{N} = \frac{1}{\cancel{N}}\frac{4}{3}\pi \underbrace{\rho_1^3}_{\text{dist. mínima}} \overbrace{\frac{N^{\cancel{2}}}{2}}^{\text{\# pares de moléculas}} = bN$$

↳ repulsión a corto alcance.

$$\cdot\; U_0 = \int \underbrace{n(r)}_{N/V} u(r)\, d^3r \approx \mathrm{vol}(\rho_{min})\cdot -u_0 \frac{N}{V} = \overbrace{-\frac{2aN}{V}}^{\text{atracción a largo alcance}}$$

- $F = -k_bT\ln Q$

$$= \underbrace{-k_bT\ln Q_{ideal}}\; - k_bTN\ln\left(1-\frac{bN}{V}\right) - \cancel{k_bT}N\cdot\left(\frac{aN}{V\cancel{k_bT}}\right)$$

- $$P = -\frac{\partial F}{\partial V} = \frac{k_bTN}{V} + \frac{k_bTN}{\left(1-\frac{bN}{V}\right)}\cdot+\frac{bN}{V^2} + -\frac{aN^2}{V^2}$$

$$= \frac{k_bTN}{V} + \frac{k_bTN^2b}{V^2}\left[1+\frac{bN}{V}+\left(\frac{bN}{V}\right)^2+\dots\right] - \frac{aN^2}{V^2}$$

↳ expansión virial.

$$\Rightarrow \left(P+\frac{aN^2}{V^2}\right) = \frac{k_bTN}{V}\left(1+\underbrace{\frac{Nb}{V-bN}}\right)$$

$$= \frac{k_bTN}{\cancel{V}}\cdot\frac{\cancel{V}}{V-bN}$$

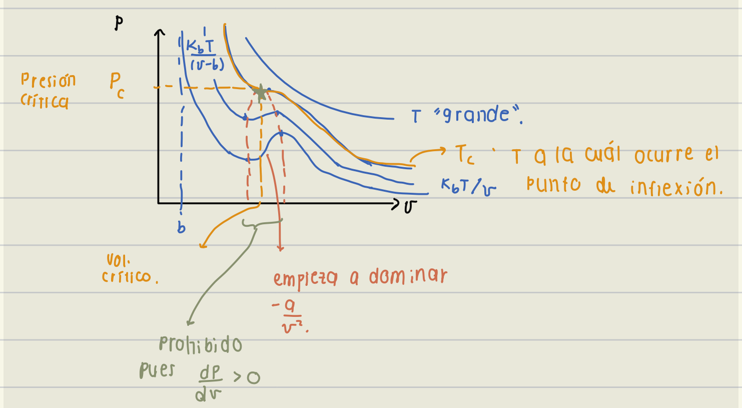
$$\Longrightarrow \boxed{\left(P+\frac{aN^2}{V^2}\right)(V-bN) = k_bTN}$$

Ec. de Estado de Van der Waals.

- $$\bar{E} = -\frac{\partial}{\partial\beta}\ln Q = \overbrace{\frac{3}{2}k_bT}^{-\frac{\partial}{\partial\beta}\ln Q_{id.}} - \frac{\partial}{\partial\beta}\left(\frac{N^2a}{V}\beta\right)$$

$$= \frac{3}{2}k_bT - \frac{N^2a}{V}$$

Isotermas de van-der-waals.



En el punto crítico:

★ $\frac{\partial^2 P}{\partial v^2} = 0$, $\frac{\partial P}{\partial v} = 0$ } dadas a y b, determinan P, V, T

$\cdot\; P = P(v)$

$$\Longrightarrow T_c = \frac{8a}{27bk_b}$$

$$v_c = 3b$$

$$P_c = \frac{a}{27b^2}$$

$$\rightarrow \boxed{\frac{P_c v_c}{k_b T_c} = \frac{3}{8}} \quad \text{ley universal}$$

$$\boxed{\left(\tilde{P}+\frac{3}{\tilde{v}^2}\right)(3\tilde{v}-1) = 8\tilde{T}} \quad ;\; \tilde{P} = \frac{P}{P_c},\; \tilde{v} = \frac{v}{v_c},\; \tilde{T} = \frac{T}{T_c}$$

Ley de los estados correspondientes

Ising $\rightarrow$ sistemas de spines $\longrightarrow$ Teoría de campo medio

$\sigma_i = \pm 1$

$$\varepsilon = -\frac{J}{2}\sum_{i\neq j}\sigma_i\sigma_j - \mu B\sum_i \sigma_i \qquad \cdot \langle\sigma\rangle \overset{def}{=} \frac{1}{N}\sum_i \sigma_i = \frac{M}{\mu N}$$

Teo. campo medio: primeros vecinos

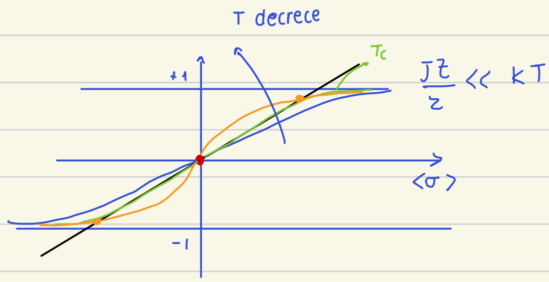
$$\varepsilon = -\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)\sum_i \sigma_i$$

$$\cdot\ (z_1)^N = \left(e^{-\beta\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)} + e^{\beta\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)}\right)^N = \left(2\cosh\left[\beta\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)\right]\right)^N$$

$$\cdot\ M = \frac{1}{\beta}\frac{\partial \ln z}{\partial B} = \frac{N}{\beta}\mu\beta\frac{\sinh\beta(\ \ )}{\cosh\beta(\ \ )} = \mu N \tanh\left(\beta\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)\right)$$

$\cdot$ con $\langle\sigma\rangle = \tanh\beta\left(\frac{Jz}{2}\langle\sigma\rangle + \mu B\right)$

$\boxed{B=0}$



En clases

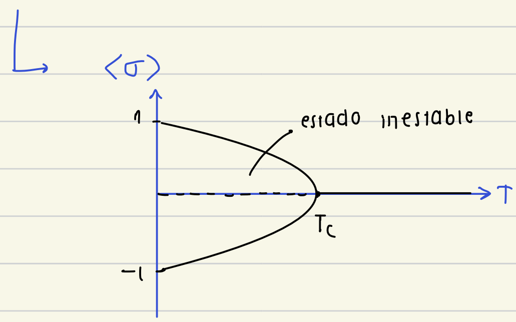
$$M = \mu g N \tanh\left(\frac{\beta\mu g}{2}\big(\overbrace{B + \alpha M}^{B_{eff}}\big)\right) \quad ; \quad m = \frac{M}{Ng\mu}$$

$$m = \tanh\Big[\underbrace{\tfrac{1}{2}\alpha(g\mu_B)^2 N}_{\equiv 1/t} m\beta\Big] \rightarrow m = \tanh\left(\frac{m}{t}\right)$$

Se obtiene Tc cuando

$$m = m/t \longrightarrow t = 1 \Rightarrow \frac{\alpha}{2}(g\mu_B)^2 N\beta = 1$$

$$\Rightarrow \boxed{\frac{\alpha}{2}(g\mu_B)^2\frac{N}{K_b} = T_c}$$



Luego, para x pequeño,

$$\tanh x \approx x - \frac{1}{3}x^3 + \dots$$

Así, $m = \frac{m}{t} - \frac{1}{3}\left(\frac{m}{t}\right)^3$

sol.

$m = 0$

$\left(\frac{1}{t} - 1\right)t^3\, 3 = m^2$, con $\frac{1}{t} \to T_c/T$

$$\sqrt{\left(\frac{T_c}{T} - 1\right)\left(\frac{T}{T_c}\right)^3 3} = m$$

$$\frac{T}{T_c}\sqrt{\left(1 - \frac{T}{T_c}\right)3} = m \longrightarrow m \propto \pm\sqrt{1 - \frac{T}{T_c}}$$

$\boxed{B\neq 0}$ $\quad m = \tanh\left[\frac{h}{t} + \frac{m}{t}\right]$, $h = \frac{H}{H_0}\cdot\frac{B}{B_0}$, $m = \frac{M}{M_0}$ $\longrightarrow$ $M_0 = Ng\mu_b$

$H_0 = \alpha g\mu_b N$

$$\cdot\ \chi = \left.\frac{\partial M}{\partial H}\right|_{H=0} = \frac{\partial h}{\partial H}\frac{\partial M}{\partial h} = \underbrace{\frac{\partial h}{\partial H}\cdot\frac{\partial M}{\partial m}}\cdot\frac{\partial m}{\partial h}$$

$$= \frac{M_0}{H_0}\left.\frac{\partial m}{\partial h}\right|_{h=0} = \frac{M_0}{H_0}\frac{\frac{\partial h}{\partial h} + \frac{\partial m}{\partial h}}{\cosh^2\left(\frac{h}{t} + \frac{m}{t}\right)}\cdot\frac{1}{t} \Longrightarrow \left.\frac{dm}{dh}\right|_{h=0} = \frac{1}{t\cosh^2\left(\frac{m}{t}\right) - 1}$$

Aleaciones Binarias → orden-desorden

- energías de enlace: $\varepsilon_{AA}, \varepsilon_{AB}, \varepsilon_{BB}$ → $E = \varepsilon_{AA} N_{AA} + \varepsilon_{AB} N_{AB} + \varepsilon_{BB} N_{BB}$.
- Número de enlaces: N_{AA}, N_{AB}, N_{BB}
- Suponemos $N_A = N_B = N/2$ → N° de part.
- z: vecinos + próximos
- $N_{AA} + N_{BB} + N_{AB} = z \cdot \frac{N}{2} = 2N_{AA} + N_{AB}$
- $N_{AA} = N_{BB} = \frac{zN}{4} - \frac{N_{AB}}{2}$

- $T=0 \to N_{AA} = N_{BB} = 0$, $\quad E = \frac{zN}{2}\varepsilon_{AB}$

Def $v = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) - \varepsilon_{AB} > 0$ → "A los A les gusta ser vecinos de los B"

Def N° de átomos en los sitios α y β.

$$N_A^\alpha = \frac{N}{4}(1+s)$$

$$N_B^\alpha = \frac{N}{2} - N_A^\alpha = \frac{N}{4}(1-s) \quad ;$$

s parámetro de orden global

$-1 \le s \le 1 \longrightarrow s = \pm 1 \to$ orden

$s = 0 \to$ desorden

Def

$$\frac{1+\sigma}{2} = \frac{N_{AB}}{N_{AA}+N_{BB}+N_{AB}} = \frac{2N_{AB}}{zN}$$

σ = parámetro de orden local

$; \quad -1 \le \sigma \le 1 \longrightarrow s = 1 \to$ orden

$s = -1 \to$ desorden.

Prob

$$P_A^\alpha = \frac{N_A^\alpha}{N/2} = \frac{1+s}{2}$$

→ $N_{AA} = \underbrace{\frac{Nz}{2}}_{\text{nº total de enlaces}} P_A^\alpha P_A^\beta = \frac{zN}{8}(1-s^2) = N_{BB}$.

Prob. que el extremo del enlace sea A.

→ $N_{AB} = \frac{Nz}{2}\left[P_A^\alpha P_B^\beta + P_A^\beta P_B^\alpha\right] = \frac{zN}{4}(1+s^2) \implies \sigma = s^2$

Def

$$E_0 \overset{def}{=} \frac{zN}{8}(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}) \longrightarrow E = E_0 - \frac{zN}{4}\sigma v$$

$$E = E_0 - \frac{zN}{4} s^2 v$$

Dado $F = -k_bT\ln Q \to Q = \sum_s e^{-\beta\varepsilon_s} = \Omega(s)\, e^{-\beta E(s)}$

$$\Omega(s) = \frac{(\frac{N}{2})!}{N_A^\alpha!\, N_B^\beta!} \cdot \frac{(\frac{N}{2})!}{N_A^\alpha!\, N_B^\beta!}$$

$\frac{N}{2}$ sitios α

$$\to F = -k_bT\left(-\beta E(s) + \ln\left(\frac{(\frac{N}{2})!^2}{(\frac{N}{4}(1-s))!^2(\frac{N}{4}(1+s))!^2}\right)\right)$$

$$= E(s) - k_bT\, 2\left[\ln\left(\frac{N}{2}\right)! - \ln\left(\frac{N}{4}(1-s)!\right) - \ln\left(\frac{N}{4}(1+s)!\right)\right]$$

$$= E(s) - \cancel{2}k_bT\left[\frac{N}{\cancel{2}}\ln\left(\frac{N}{2}\right) - \frac{N}{\cancel{4}_2}(1-s)\ln\left(\frac{N}{4}(1-s)\right) - \frac{N}{\cancel{4}_2}(1+s)\ln\left(\frac{N}{4}(1+s)\right)\right]$$

$$= E(s) - k_bTN\left[\ln\left(\frac{N}{2}\right) - \frac{(1-s)}{2}\ln\left(\frac{N}{4}(1-s)\right) - \frac{(1+s)}{2}\ln\left(\frac{N}{4}(1+s)\right)\right]$$

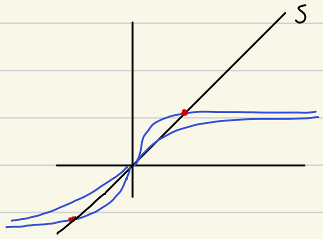
Minimizando F: T y V cte.

$$0 = \frac{\partial F}{\partial s} = \frac{\partial E(s)}{\partial s} - k_b T N \left[+ \frac{1}{2} \ln\left(\frac{N}{4}(1-s)\right) - \cancel{\frac{(1-s)}{2} \frac{4}{N} \frac{1}{(1-s)}} \cdot (-1) - \frac{1}{2} \ln\left(\frac{N}{4}(1+s)\right) - \cancel{\frac{(1+s)}{2} \frac{4}{N} \frac{1}{(1+s)}} \right]$$

$$0 = \frac{z\cancel{N}}{2} s v - k_b T \cancel{N} \left[\frac{1}{2} \ln\left(\frac{1-s}{1+s}\right) \right]$$

$$\Rightarrow \left[s = \frac{\cancel{2} k_b T}{v z \cancel{2}} \ln\left(\frac{1-s}{1+s}\right) \right] \Rightarrow \left[s = \tanh \frac{z v s}{2 k_b T} \right]$$

Solución



$s \neq 0$ si $T < T_c = \frac{zv}{2k_b}$

$\downarrow$

$s = s_m$

cap. calórica

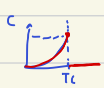
$C = \frac{\partial E}{\partial T}$; $\bar{E} = E_0 - \frac{zN}{4} v \overline{s^2}$; $\overline{s^2} \approx s_m^2$ $(\bar{s}_m^2)$

$\uparrow$

despreciar las fluctuaciones.

$\rightarrow \bar{E} \simeq E_0 - \frac{zN}{4} v s_m^2$

$\rightarrow C = -\frac{zN}{4} v \, \partial s_m^2 / \partial T$ $\begin{cases} 0 , & T > T_c \\ \text{} & T < T_0 \end{cases}$



* transiciones de 1° orden: var termodinámicas como V, M o S discontinuas.

" " 2° orden: derivadas discontinuas $\longrightarrow$ χ o C_v