Microscopic Models

multiplicity of macrostates

Entropy (equally probable)
- fundamental assumption
- laws of probabilities

- Two-State Paramagnet
- Einstein Solid
- Monatomic Ideal Gas

$\xrightarrow[\text{mechanics}]{\text{quantum}}$

$$\Omega(N)=2^N;\quad \Omega(N,N_\uparrow)=\binom{N}{N_\uparrow}$$

$$\Omega(N,q)=\binom{q+N-1}{q}$$

$$\Omega(N,U,V)=f(N)V^N U^{\frac{3N}{2}}$$

$$\longrightarrow S = k\ln\Omega$$

Why there is an equilibrium state?

① Statistical Mechanics

What equilibrium state is. Ω. Ω_{max}

Rates of Process: transport of {energy, momentum, particles}

③ Transport Theory / Kinetics.

How long to reach equilibrium.

What equilibrium state is {Thermal, Mechanical, Diffusive}

② Classical Thermodynamics

$$S = S(U,V,N)$$

$$dS=\left(\frac{\partial S}{\partial U}\right)_{V,N}dU+\left(\frac{\partial S}{\partial V}\right)_{N,U}dV+\left(\frac{\partial S}{\partial N}\right)_{U,V}dN$$

$$dS=\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dN$$

Governing Variable

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{V,N}\qquad \frac{P}{T}=\left(\frac{\partial S}{\partial V}\right)_{N,U}\qquad \frac{\mu}{T}=-\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Exchanged Quantity: Energy | Volume | Particles

Type of interaction: Thermal | Mechanical | Diffusive

$S=k\ln\Omega \longrightarrow$

$S(U,V,N)=S$

$$T=\left(\frac{\partial S}{\partial U}\right)^{-1}\longrightarrow \begin{cases}\mu=-T\left(\frac{\partial S}{\partial N}\right)\\ P=T\left(\frac{\partial S}{\partial V}\right)\end{cases}$$

$$H=U+PV$$

$$\longrightarrow \begin{cases}C_V=\left(\frac{\partial U}{\partial T}\right)_V\\ C_P=\left(\frac{\partial H}{\partial T}\right)_P=\left(\frac{\partial (U+PV)}{\partial T}\right)_P=\left(\frac{\partial U}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P\end{cases}$$

Microscopic Models

I. Ideal Gas (Monatomic)

1. $$\Omega(N,U,V) = \frac{1}{N!}\frac{V^N \cdot V_p}{(h^3)^N} = \frac{1}{N!}\frac{V^N \cdot A_{3N}(\sqrt{2mU})}{(h^3)^N}$$

$$A_{3N}(\sqrt{2mU}) = \frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)}\left(\sqrt{2mU}\right)^{3N-1} = \frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}\left(\sqrt{2mU}\right)^{3N-1}$$

radius $= \sqrt{2mU}$:

(dimension $= 3N$: $p_{1x}^2+p_{1y}^2+p_{1z}^2+\cdots+p_{Nx}^2+p_{Ny}^2+p_{Nz}^2 = 2mU$.)

(1) $$\Omega(N,U,V) = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}\left(\sqrt{2mU}\right)^{3N-1} \approx \boxed{\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\left(\sqrt{2mU}\right)^{3N}}$$ ①

$$\approx \left[\frac{V}{N}\cdot\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\cdot e^{\frac{5}{2}}\right]^N$$ Stirling's approximation

(2) ② $$\boxed{S = k\ln\Omega = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right)+\frac{5}{2}\right]}$$

* ① $$\boxed{\Omega(N,U,V) = f(N)\cdot V^N \cdot U^{\frac{3N}{2}}}$$

② $$\boxed{S = k\ln\Omega = Nk\ln V + \frac{3}{2}Nk\ln U + k\ln f(N)}$$

2. $$T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{\frac{3}{2}Nk}{U}\right)^{-1} \Leftrightarrow U = \frac{3}{2}NkT$$

3. $$P = T\left(\frac{\partial S}{\partial V}\right) = T\cdot\frac{Nk}{V} \Leftrightarrow PV = NkT$$

4. $$\mu = -T\frac{\partial S}{\partial N} = -Tk\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right) = -Tk\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right)$$

5. $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk.$$

6. $$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p = C_V + Nk = \frac{5}{2}Nk$$

for ideal gas

Ⅱ. Einstein Solid.

1. $\Omega(N,q) = \binom{N+q-1}{q} = \frac{(N+q-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q!\,N!}$; $U = q\varepsilon$.

(1) $\frac{(q+N)!}{q!N!} \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{\frac{2\pi q(q+N)}{N}}} \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \approx \begin{cases} \left(\frac{eq}{N}\right)^N, & q \gg N \\ \left(\frac{eN}{q}\right)^q, & N \gg q \end{cases}$

stirling approximation

logrithm ↓ ... logrithm ↓ stirling approximation

(2) ① $\ln\Omega = \ln(q+N)! - \ln q! - \ln N! \approx (q+N)\ln(q+N) - q\ln q - N\ln N$

② $S = k\ln\Omega = k[(q+N)\ln(q+N) - q\ln q - N\ln N]$

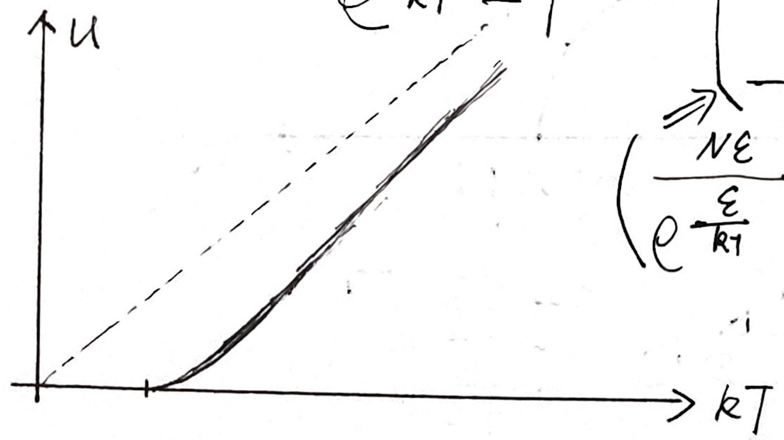
$= Nk\left(\ln\left(\frac{q}{N}\right)+1\right)$, $q \gg N$, high temperature

$= qk\left(\ln\left(\frac{N}{q}\right)+1\right)$, $N \gg q$, low temperature

2. $T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{\partial S}{\partial q}\frac{dq}{dU}\right)^{-1} = \left(\frac{\partial S}{\partial q}\frac{1}{\varepsilon}\right)^{-1} = \left[\frac{k}{\varepsilon}\ln\left(\frac{U+\varepsilon N}{U}\right)\right]^{-1}$

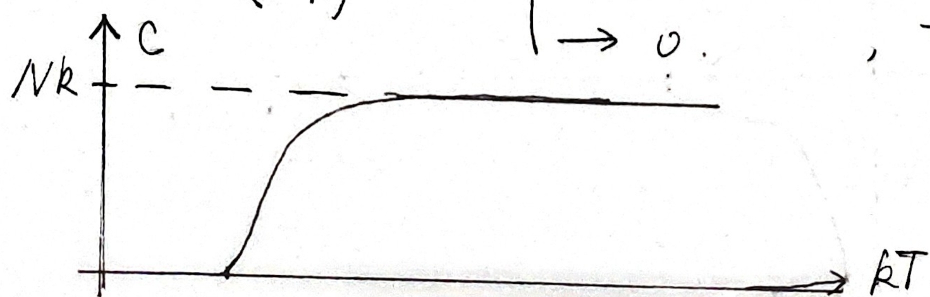
$\Leftrightarrow U = \frac{N\varepsilon}{e^{\frac{\varepsilon}{kT}}-1} \begin{cases} \to NkT, & T \to +\infty \\ \to 0, & T \to 0 \end{cases}$

$\Rightarrow \left(\frac{N\varepsilon}{e^{\frac{\varepsilon}{kT}}} = N\varepsilon \cdot e^{-\frac{\varepsilon}{kT}}\right)$



3. $\mu = -T\left(\frac{\partial S}{\partial N}\right) = -kT\ln\left(\frac{N+q}{N}\right) = \begin{cases} \to -kT\left(\frac{q}{N}\right), & T \to 0 \\ \to +\infty, & T \to +\infty \end{cases}$

4. $C = \left(\frac{\partial U}{\partial T}\right) = \begin{cases} \to Nk, & T \to +\infty \\ \to 0, & T \to 0 \end{cases}$



Ⅲ Two State Paramagnet

1. N as a constant. $N = N\uparrow + N\downarrow$. $\propto \vec{J}$

$\vec{\mu}$: megnetic moment vector

$\mu_z = \vec{\mu} \cdot \frac{\vec{B}}{|\vec{B}|} = \pm \mu$

(1) $\Omega(N\uparrow) = \binom{N}{N\uparrow} = \frac{N!}{N\uparrow! \, N\downarrow!}$

(2) ① $\ln \Omega(N\uparrow) \approx N \ln N - N\uparrow \ln N\uparrow - N\downarrow \ln N\downarrow$

energy

* $U = \mu B (N\downarrow - N\uparrow) = \mu B (N - 2N\uparrow)$. $\mu = |\mu_z|$

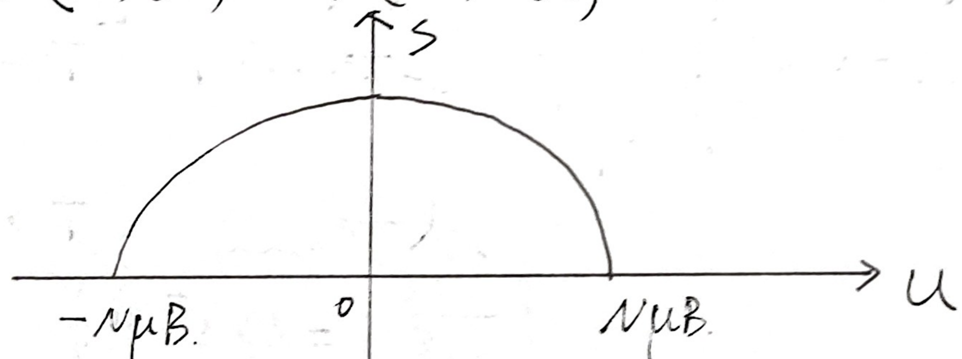
* $M = \mu (N\uparrow - N\downarrow) = -\frac{U}{B}$ megnetization

For One particle (dipole): $\begin{cases} U = -\vec{\mu} \cdot \vec{B} = -\mu_z B = \begin{cases} -\mu B, & \uparrow \\ \mu B, & \downarrow \end{cases} \\ M = \vec{\mu} \cdot \frac{\vec{B}}{|\vec{B}|} = \mu_z = \begin{cases} \mu, & \uparrow \\ -\mu, & \downarrow \end{cases} \end{cases}$

②

$$S = k \ln \Omega(N\uparrow) = k\left[N \ln N - \left(\frac{N - \frac{U}{\mu B}}{2}\right) \ln \left(\frac{N - \frac{U}{\mu B}}{2}\right) - \left(\frac{N + \frac{U}{\mu B}}{2}\right) \ln \left(\frac{N + \frac{U}{\mu B}}{2}\right)\right]$$

$$S = S(N, U) = S(N, -U)$$

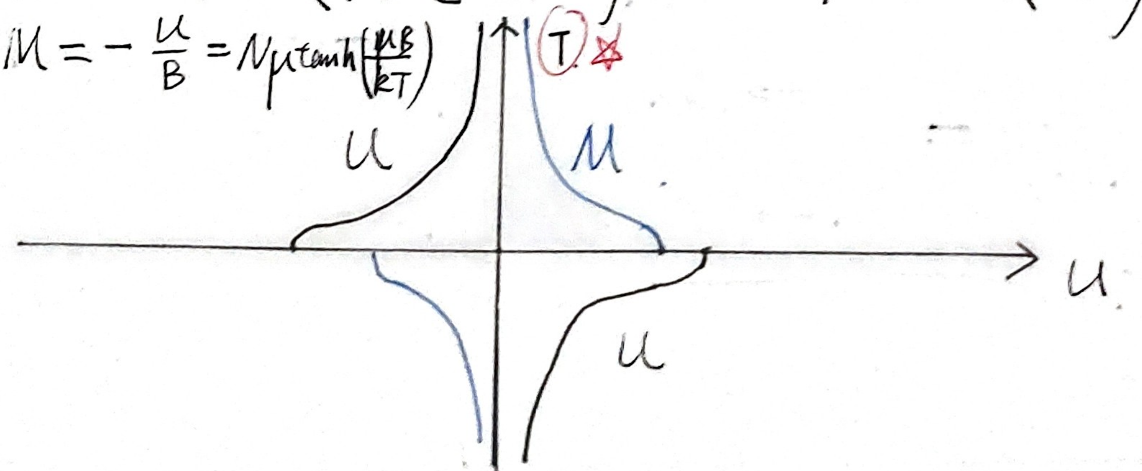


2. $T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{k}{2\mu B} \ln \frac{N - \frac{U}{\mu B}}{N + \frac{U}{\mu B}}\right)^{-1}$

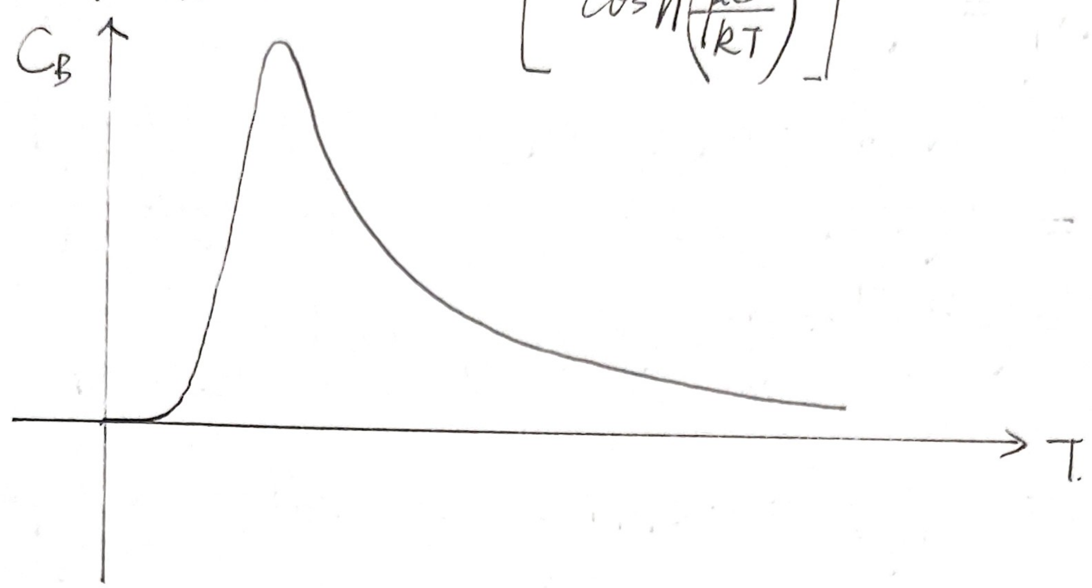
$\Updownarrow$

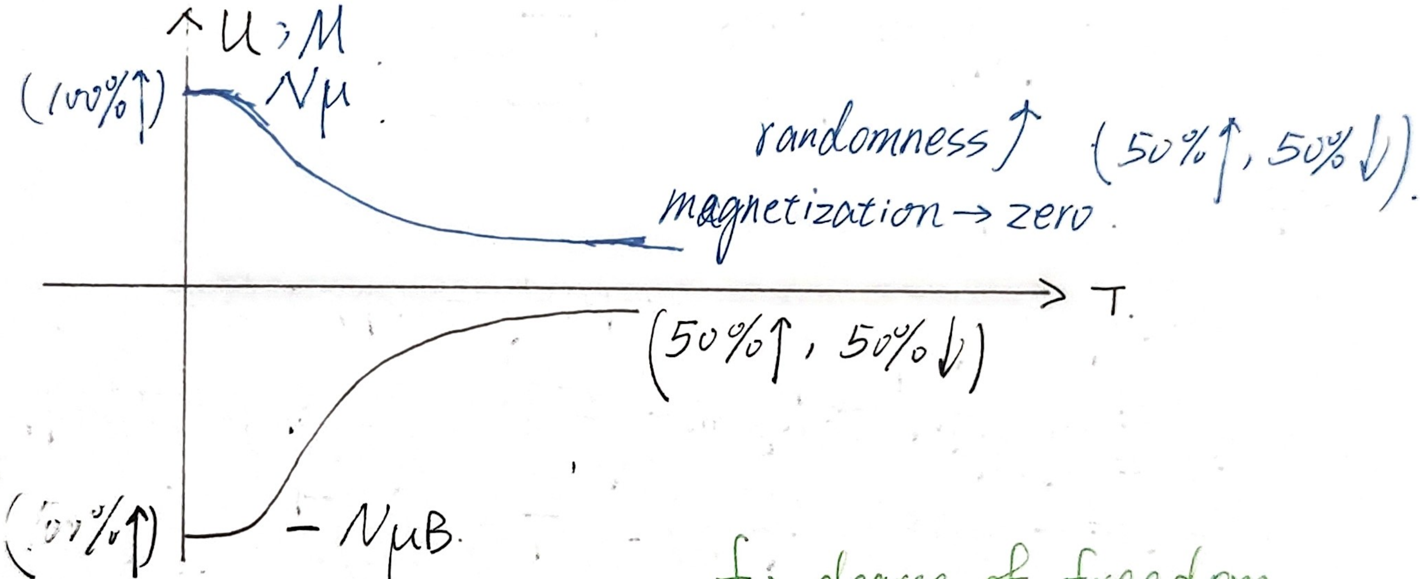
$$U = N\mu B \left(\frac{1 - e^{-\frac{2\mu B}{kT}}}{1 + e^{\frac{2\mu B}{kT}}}\right) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

$M = -\frac{U}{B} = N\mu \tanh\left(\frac{\mu B}{kT}\right)$



3. $C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk\left[\frac{\frac{\mu B}{kT}}{\cosh\left(\frac{\mu B}{kT}\right)}\right]^2$





f: degree of freedom.

IV Conclusion.

1. Monatomic Ideal Gas.

$$\begin{cases} U = \frac{f}{2}NkT \\ C_V = \frac{f}{2}Nk \end{cases}$$

① $\Omega(N, U, V) = f(N)\, V^N U^{\frac{3N}{2}}$

② $S = k\ln\Omega = Nk\ln V + \frac{3}{2}Nk\ln U + k\ln f(N)$

③ $U = \frac{3}{2}NkT$; $T = \left(\frac{\partial S}{\partial U}\right)^{-1}$ varified equipartition theorem

④ $PV = NkT$; $P = T\left(\frac{\partial S}{\partial V}\right) = -\left(\frac{\partial U}{\partial V}\right)$

⑤ $\mu = -Tk\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right)$; $\mu = -T\left(\frac{\partial S}{\partial N}\right) = \left(\frac{\partial U}{\partial N}\right)$

⑥ $C_V = \frac{3}{2}Nk = \left(\frac{\partial U}{\partial T}\right)_V$.

⑦ $C_P = C_V + Nk = \frac{5}{2}Nk = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

2. Einstein Solid.

$$\begin{cases} U = \frac{f}{2}NkT \\ C_V = \frac{f}{2}Nk \end{cases}$$

① $\Omega(N,q) = \binom{N+q-1}{q}$

② $S = k\ln\Omega(N,q) = k\left[(q+N)\ln(q+N) - q\ln q - N\ln N\right]$

$\Downarrow$

$S = S(N,U)$, $U = q\varepsilon$. f: degree of freedom.

③ $T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left[\frac{k}{\varepsilon}\ln\left(\frac{U+\varepsilon N}{U}\right)\right]^{-1}$; $U = \frac{N\varepsilon}{e^{\frac{\varepsilon}{kT}}-1} = \begin{cases} NkT, & T\to+\infty \\ 0, & T\to 0 \end{cases}$

④ $\mu = -T\left(\frac{\partial S}{\partial N}\right) = -kT\ln\left(\frac{N+q}{N}\right)$ varified equipartion theorem.

⑤ $C = \left(\frac{\partial U}{\partial T}\right) = \begin{cases} Nk, & T\to+\infty. \\ 0, & T\to 0. \end{cases}$

3. Two State Paramagnet.

① $\Omega(N\uparrow) = \binom{N}{N\uparrow}$; $U = \mu B(N-2N\uparrow)$; $M = -\frac{U}{B}$.

② $S = k\ln\Omega(N\uparrow) = k\left[N\ln N - \left(\frac{N-\frac{U}{\mu B}}{2}\right)\ln\left(\frac{N-\frac{U}{\mu B}}{2}\right) - \left(\frac{N+\frac{U}{\mu B}}{2}\right)\ln\left(\frac{N+\frac{U}{\mu B}}{2}\right)\right]$

$\Downarrow S = S(N,U)$

③ $U = -N\mu B\tanh\left(\frac{\mu B}{kT}\right)$ $T = \left(\frac{\partial S}{\partial U}\right)^{-1}$

$M = -\frac{U}{B} = N\mu\tanh\left(\frac{\mu B}{kT}\right)$.

④ $C_B = \left(\frac{\partial U}{\partial T}\right)_{B,N} = Nk\left[\frac{\frac{\mu B}{kT}}{\cosh\left(\frac{\mu B}{kT}\right)}\right]^2$.

$$\begin{cases} U = U(T,N,V) \\ \Updownarrow \\ T = T(N,U,V) \end{cases}$$

$$\Omega = \Omega(N,U,V) \xrightarrow{S = k\ln\Omega} S = S(N,U,V) \rightarrow \begin{cases} P = P(N,V,T) \\ \mu = \mu(N,V,T). \end{cases}$$

$$\begin{cases} C_V = C_V(T,N,V) \\ C_P = C_P(T,N,V) \\ C_B = C_B(T,N,V) \end{cases}$$

Usually

$U = U(T,N)$.

$C = C(T,N)$

Especially

$U = U(T,N) = \frac{f}{2}NkT$

$C = C(N) = \frac{f}{2}Nk$.

$\Downarrow$

Equipartition Theorem.