for microcanonical only

bridge (Based on Boltzmann's definition)

Microcanonical: $P_{"i"} \to \underline{S = k_B \ln W} \to$ All (Thermodynamics)

Canonical: $P_{"i"} \to$??? Bridge $\to$ All (Thermodynamics)

Thermodynamics (Review or Preview)

1. Entropy redefined

General Def: $S = -k_B \sum P_{"i"} \ln P_{"i"}$ (general definition)

Homework: if we use $P_{"i"}(\text{microcanonical}) = \begin{cases} a, & \text{if} \cdots \\ 0, & \text{otherwise} \end{cases}$ (*),

then $S = k_B \ln W$ is recovered.

Now in canonical ensemble, $S = k_B \ln Z + \langle E \rangle / T$

Pf: $P_{"i"} = \frac{1}{Z} e^{-\beta E_{"i"}} \Rightarrow \ln P_{"i"} = -\ln Z - \beta E_{"i"}$

According to (*), $S = -k_B [\sum -P_{"i"} \ln Z + \sum P_{"i"} (-\beta E_{"i"})]$

which one?

$= k_B \ln Z + \frac{1}{T} \sum P_{"i"} E_{"i"} = k_B \ln Z + \frac{\langle E \rangle}{T}$

2. Thermodynamics

$1^{st} + 2^{nd}$ laws: $\overset{\text{internal energy}}{dU} = \underset{\text{heat transfer}}{TdS} - \underset{\text{work done}}{pdV} + \overset{\text{chemical potential variation}}{\mu dN}$

$dS = T^{-1} dU + pT dV - \mu T dN$ (just rewrite)

internal energy (= total energy E)

Microcanonical $dU = TdS - pdV + \mu dN$

$dS = T^{-1} d\underline{E} + pT^{-1} d\underline{V} - \mu T^{-1} d\underline{N}$ $S = S(E, V, N)$

Canonical Introduce Helmholtz free energy

$F(T, V, N) = E - TS$ $F = F(T, V, N)$

$dF \underset{\text{math identity}}{=} dE - TdS - SdT \underset{\text{1st \& 2nd laws}}{=} -SdT - pdV + \mu dN$

Going from one set of variables → another Legendre Transformation

In Stat. Mech.

$$\boxed{F} = E - T[\underbrace{k_B \ln Z + \bar{E}/T}_{\text{entropy}}] = -k_B T \ln Z$$

Bridge

partition function

3. Ideal Gas

$$H[\vec{r}^N, \vec{p}^N] = \frac{1}{2m}\sum_j \vec{p}_j^{\,2} + \text{potential energy } 0 \text{ for ideal gas}$$

$$Z = \int d\vec{r}^N d\vec{p}^N \exp\left(-\frac{\beta}{2m}\sum_j p_j^2\right)$$

Gaussian Integral $\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

$$\boxed{= V^N \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3N} = Z(V, T, N)}$$

partition function for ideal gas

$$F = -k_B T \ln Z \qquad -P = \frac{\partial F}{\partial V} = -k_B T\left(\frac{\partial(\ln Z)}{\partial V}\right)_{T,N} = -\frac{k_B T}{Z}\frac{\partial Z}{\partial V} = -\frac{k_B T}{V^N}\cdot N V^{N-1}$$

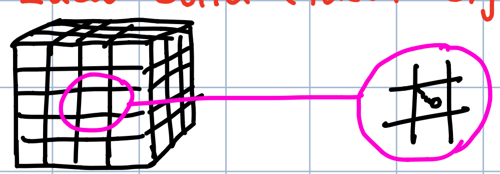
$$= -\frac{N k_B T}{V} \Rightarrow PV = N k_B T$$

Equation of State for Ideal gas

$$\langle E \rangle = \bar{E} = -\left(\frac{\partial(\ln Z)}{\partial \beta}\right)_{N,V} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{N,V} = +\frac{3N}{2\beta} = +\frac{3N k_B T}{2}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \frac{1}{Z}\left(\frac{\partial Z}{\partial N}\right)_{\beta,V} = -k_B T \ln\left(V\cdot\left(\frac{2\pi m}{\beta}\right)^{3/2}\right)$$

§ 8 Ideal Solid (ideal crystal)



1. Model: $H(\vec{r}^N, \vec{p}^N) = \frac{1}{2m}\sum_j \vec{p}_j^{\,2} + \sum_j V(\vec{r}_j)$

can be diagnonized

$$V(\vec{r}_j) = V(0) + \underbrace{\nabla_{\vec{r}_j} V(\vec{r}_j)\Big|_{\vec{r}=0}}_{\substack{\text{Force at equilibrium} \\ =0}} \cdot \vec{r}_j + \frac{1}{2}\sum \frac{\partial^2 V(\vec{r}_j)}{\partial r_m \partial r_n}\Big|_{\vec{r}_j=0} \cdot r_m \cdot r_n$$

$$= V(0) + \frac{1}{2}\frac{\partial^2 V}{\partial x^2}\cdot x^2 + \frac{1}{2}\frac{\partial^2 V}{\partial y^2} y^2 + \frac{1}{2}\frac{\partial^2 V}{\partial z^2} z^2.$$

K (for simplicity)

$$= \frac{1}{2m}\sum_j \vec{p}_j^{\,2} + \frac{K}{2}\sum_j \vec{r}_j^{\,2}$$

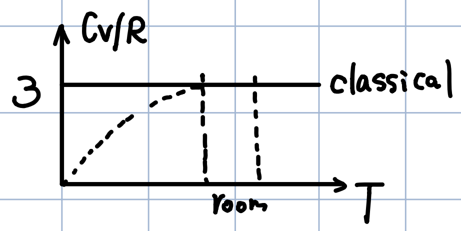
2. Classical Theory

$$Z = \int d\vec{r}^N d\vec{p}^N \exp\left(-\beta \frac{1}{2m}\sum_j \vec{P}_j^2 - \beta \cdot \frac{k}{2}\sum_j \vec{r}_j^2\right)$$

$$= \left(\frac{2\pi m}{\beta}\right)^{3N/2}\left(\frac{2\pi}{\beta K}\right)^{3N/2} = (2\pi)^{3N}\cdot \beta^{-3N}\cdot\left(\frac{m}{k}\right)^{3N/2}$$

$$\Rightarrow \langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{\beta} = 3Nk_BT$$

$C_v = \frac{\partial\langle E\rangle}{\partial T} = \underline{3Nk_B}$ for ideal solid (no m, no k) universal !



How good is this theoritical result ?

Very good ! (some exceptions)

3. Einstein's Theory

H(classical) SHO

$$H = \frac{1}{2m}\sum \vec{P}_j^2 + \frac{1}{2}\sum \vec{r}_j^2 = \left(\frac{1}{2m}P_{1x}^2 + \frac{k}{2}x_1^2\right) + \cdots$$

QM: $E_{\text{"}i\text{"}} = E(n_1, n_2, \cdots, n_{3N}) = \hbar\omega(n_1 + \frac{1}{2}) + \hbar\omega(n_2 + \frac{1}{2}) + \cdots$

$(n_1, n_2, \cdots, n_{3N})$ represent a Quantum state

$$= \sum_{k=1}^{3N} \hbar\omega\cdot(n_k + \tfrac{1}{2})$$

ω_E (Einstein)

$$Z = \sum e^{-\beta E_{\text{"}i\text{"}}} = \sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots\sum_{n_{3N}} e^{-\beta\hbar\omega\left(\frac{3N}{2} + n_1 + n_2 + \cdots + n_{3N}\right)}$$

$$= \sum_{n_1} e^{-\beta\hbar\omega(\frac{1}{2} + n_1)} \cdot \cdots\cdots \sum_{n_{3N}} e^{-\beta\hbar\omega(\frac{1}{2} + n_{3N})}$$

$$= \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\right)^{3N} \equiv z_1^{3N} \qquad z_1 = \frac{1}{2\sinh(\beta\hbar\omega/2)} \qquad Z = \left[\frac{1}{2\sinh(\beta\hbar\omega/2)}\right]^{3N}$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{+\beta\hbar\omega} - 1}\right)$$

$$C_v = \frac{\partial \bar{E}}{\partial T} = \underbrace{3Nk_B}_{\text{classical}} \cdot \boxed{\frac{x^2 e^x}{(e^x - 1)^2}} \qquad x \equiv \beta\hbar\omega$$

T dependent

material dependent

Limiting cases: 1° small $x \Leftrightarrow$ high T & small $\hbar\omega \to 3Nk_B$

2° large $x \Leftrightarrow$ low T & large $\hbar\omega \to 0$

3°. Generally