① (T, V, N) "Theoretical Interpretation"

For OPEN SYSTEM ⟶ CAN Exchange Energy with Environment

↳ S not always MAX

↳ F is MIN if T LOW

ORDERED STATE may result, or preferred

Living things

② "Practical USE" — Z easier to calc than Ω

Consider Einstein Solid

↳ N Harmonic Oscillators.

— Microstates are q_1 - - - - - - q_n $(q_i > 0)$

quantum of energy

– Energy of μstates $E(q_1 \cdots\cdots q_N)$

$$= \hbar\omega(q_1 + \cdots\cdots + q_N)$$

$$= \hbar\omega q_1 + \hbar\omega q_2 + \cdots\cdots + \hbar\omega q_N$$

– $$Z_{\substack{\text{EINSTEIN}\\ \text{SOLID}}} = \sum_{s}{}' e^{-E_s/kT}$$

$s \longleftarrow$ μ states

$$= \underbrace{\sum_{q_1=0}^{\infty} \sum_{q_2=0}^{\infty} \cdots\cdots \sum_{q_N=0}^{\infty}} e^{-\frac{\hbar\omega q_1 + \cdots\cdots + \hbar\omega q_N}{kT}}$$

S is collective label for all quantum numbers

$$= \sum_{q_1=0}^{\infty} \sum_{q_2=0}^{\infty} \cdots\cdots \sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega q_1}{kT}} \cdot e^{-\frac{\hbar\omega q_2}{kT}} \cdots\cdots \cdot e^{-\frac{\hbar\omega q_N}{kT}}$$

$$= \underbrace{\left(\sum_{q_1=0}^{\infty} e^{-\hbar\omega/kT \cdot q_1}\right)}_{\text{Z for single harmonic Oscillator}} \underbrace{\left(\sum_{q_2=0}^{\infty} e^{-\frac{\hbar\omega}{kT} q_2}\right)}_{\text{Z for single Harmonic Oscillator}} \cdots \left(\sum_{q_N=0}^{\infty} e^{-\frac{\hbar\omega}{kT} q_N}\right)$$

same

So

$$Z_{\substack{\text{EINSTEIN}\\ \text{SOLID}\\ N\text{-OSC}}} = \left(Z_1\right)^N$$

Partition function of a Single Osc.

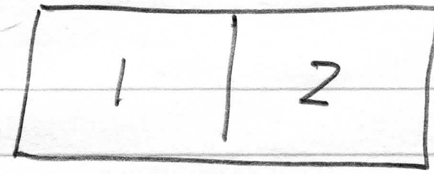
$$Z_1 = \sum_{q=0}^{\infty} e^{-\hbar\omega/kT \cdot q}$$

→ GEOMETRIC SERIES

$$\sum_{n=0}^{\infty} \alpha^n = \frac{1}{1-\alpha} \qquad |\alpha| < 1$$

$$Z_1 = \frac{1}{1 - e^{-\hbar\omega/kT}}$$ Einstein Solid

Generally



System $E = E_1 + E_2$

then $Z = \underbrace{Z_1 \times Z_2}$

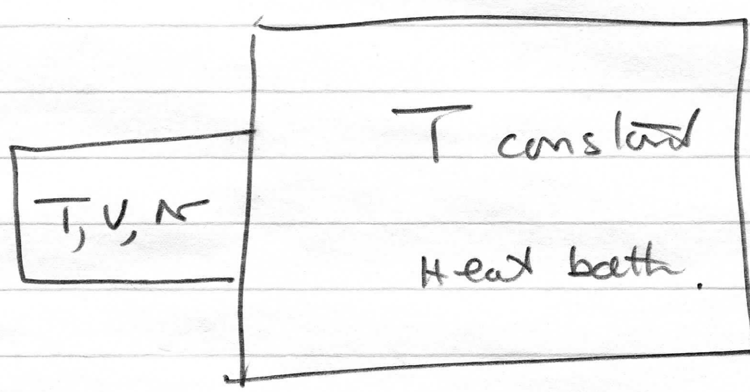
partition function of combined system

product of partition functions on subsys

↳ IFF Energies Additi

↳ i.e. subsys do not interact

→ TECHNICAL ADVANTAGE of Viewing system as



LEAVE ON BOARD

Still Einstein Solid

$$Z_N = (Z_1)^N \; ; \quad Z_1 = \frac{1}{1 - e^{-\hbar\omega/kT}}$$

OR using $\frac{1}{1-x} = 1 + x + x^2 + x^3 \ldots$

$$Z_1 = 1 + e^{-\hbar\omega/kT} + e^{-2\hbar\omega/kT} + e^{-3\hbar\omega/kT} + \ldots$$

$$Z_1 = e^{-E_0/kT} + e^{-E_1/kT} + e^{-E_2/kT} + \ldots$$

PARTITION FUNCTION

AT given T μ STATES PARTITIONED

whether or not they contribute to Z_1

– AT given kT, STATES with $E \gg kT$ do not contribute

Contrib exponentially suppressed

$$e^{-E/kT} \ll 1$$

States with $E << kT$ contribute

Essentially UNITY ($E/kT << 1$) to Z

↳ ALSO CONTRIBUTE TO F

↳ AND SO TO $S, P, \mu \rightarrow F = -kT \ln Z$

partial derivatives

— at $T \rightarrow 0$, $Z \approx e^{-E_0/kT}$

↳ All states $E > E_0$ suppressed.

$$Z = e^{-E_0/kT}\left(1 + e^{-(E_1-E_0)/kT} + e^{-(E_2-E_0)/kT} + \cdots\right)$$

$$Z \approx e^{-E_0/kT}$$

when $T \rightarrow 0$, this $\rightarrow 0$

since $E_1 > E_0$

$e^{-(\text{very large})}$

$\longrightarrow 0$

Can always define E_0 as 0

So $\rightarrow$ E_0, $Z \rightarrow 1$ as $T \rightarrow 0$

or $Z = e^{-E_0/kT} = 1$

OTHER HAND as $T \to \infty$ ALL μSTATES

CONTRIBUTE UNITY

↳ $Z \to$ TOTAL # μ STATES

$\Rightarrow Z$ goes 1 at $T = 0$

to

μSTATES as $T \to \infty$

– Intermediate T, $Z \propto$ # μSTATES which contribute to thermo Dynamic Equilibrium

μ STATES important in determining S, P, μ

→ AT given T only a FINITE # of μSTATE (N finite) are important

↳ those with $E \lesssim kT$.

THIS IS IMPORTANT FEATURE of ALL PHYSICS

- At a given energy scale (eg kT)

Physics at energy scales $\gg kT$

↳ NOT relevant in describing phenomena at scales $\ll kT$

EG. Do not need to understand

NUCLEAR PHYSICS to study an

IDeal gas at room Temp

Nuclear PHYSICS — MeV 10^6

gas at room Temp — eV

- DO not care about quark, string, etc ~~structure~~ of proton.

↳ Kenneth Wilson

↳ if not true would have to understand EVERYTHING. before making progress.

Again back to Einstein Solid.

$$Z = \left(\frac{1}{1 - e^{-\hbar\omega/kT}} \right)^N$$

SHOULD BE ON BOARD

$$\& \; P(E_s) = \frac{1}{Z} e^{-E_s/kT}$$

any μstate

— IF have PROBABILITY, can calculate AVERAGES

By Definition $\langle E \rangle = \sum_s E_s (P_s)$

μSTATES

average value of Energy of System @ T

$$\langle E \rangle = \sum_s E_s (P_s)$$

$$= \frac{1}{Z} \sum_s E_s e^{-E_s/kT}$$

KEEP ON BOARD

note → $$-\frac{\partial}{\partial a} \sum e^{-aE_s} = \sum E_s e^{-aE_s}$$

so $$= \frac{1}{Z} \frac{\partial}{\partial(-\frac{1}{kT})} \sum_s e^{-E_s/kT}$$

$$= \frac{1}{Z} \frac{\partial}{\partial(-\frac{1}{kT})} \cdot Z$$

$$\langle E \rangle = \frac{\partial}{\partial(-\frac{1}{kT})} \ln Z$$

$$\left\{ \begin{aligned} \partial\left(-\frac{1}{kT}\right) &= \cancel{\partial(-1) \cdot \frac{1}{kT}} + \partial\left(\frac{1}{kT}\right)(-1) \\ &= -\frac{1}{kT^2} \frac{\partial}{\partial T} (-1) \end{aligned} \right.$$

$$\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln Z$$

can write this as $\frac{1}{kT} \equiv \beta$

$$Z = \sum_s e^{-\beta E_s}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

For Einstein Solid

$$Z = \left(1 - e^{-\hbar\omega/kT}\right)^{-N}$$

$$= \left(1 - e^{-\beta\hbar\omega}\right)^{-N}$$

showed $\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z$

$$= -\frac{\partial}{\partial\beta} \ln\left(1 - e^{-\beta\hbar\omega}\right)^{-N}$$

$$= N\frac{\partial}{\partial\beta} \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= \frac{N}{(1-e^{-\beta\hbar\omega})} \frac{\partial}{\partial\beta}\left(-e^{-\beta\hbar\omega}\right)$$

$$= \frac{N\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{N\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$\langle E \rangle = \frac{\hbar\omega N}{e^{\hbar\omega/kT}-1}$$

Can use this to calc Heat Capacity C.

$$\frac{\langle E \rangle}{N} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$$

$kT \ll \hbar\omega$

$$\frac{\langle E \rangle}{N} \approx \hbar\omega\, e^{-\hbar\omega/kT}$$

Average Energy per Osc. $\approx \hbar\omega\, e^{-\hbar\omega/kT}$

Heat Capacity Exponentially Small as $T \to 0$

$kT \gg \hbar\omega$

$$\langle E \rangle = \frac{\hbar\omega}{\frac{\hbar\omega}{kT}\left(1 + \cdots\right)}$$

$\approx kT$

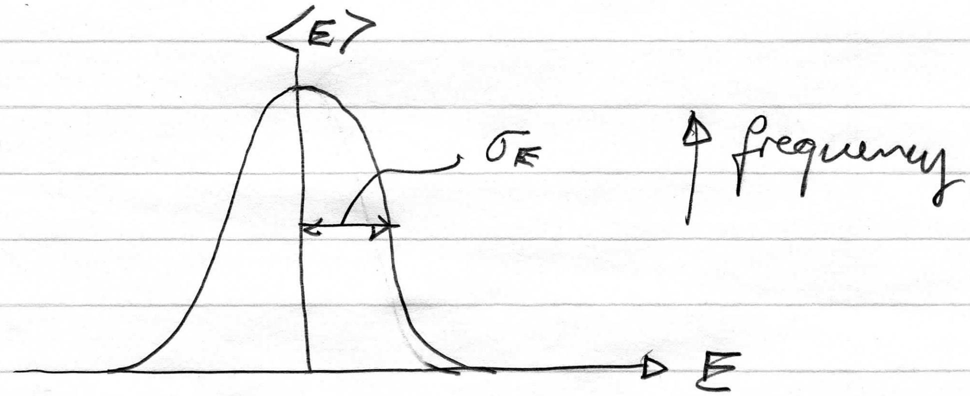
Average Energy per Oscillator $\approx kT$

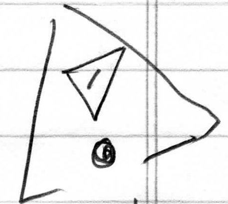
Heat Capacity $\approx NkT$ as $T \gg \frac{\hbar\omega}{k}$

Equipartition

Calculated $\langle E \rangle$ ← average energy

Can also calculation variation about MEAN





maybe skip

$$\langle E \rangle = \frac{-\partial}{\partial \beta} \ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

from STATISTICS $\langle E^2 \rangle - \langle E \rangle^2 = \sigma_E^2$

EASY

Derive

$$\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta^2} \sum_s e^{-\beta E(s)}$$

$$= \sum_s \frac{\partial}{\partial \beta^2}\left(e^{-\beta E(s)} \right)$$

$$= \sum \frac{\partial}{\partial \beta}\left(-E e^{-\beta E} \right)$$

$$= \sum_s \left[E(s) \right]^2 e^{-\beta E}$$

$$\frac{\partial^2 Z}{\partial \beta^2} = Z \cdot \sum [E(s)]^2 \frac{e^{-\beta E_s}}{Z}$$

Already showed $\langle E \rangle = \frac{1}{Z} \sum_s E_s e^{-E_s/kT}$

$$= \sum_s \frac{E_s e^{-\beta E_s}}{Z}$$

so

$$Z \langle E^2 \rangle = \frac{\partial^2 Z}{\partial \beta^2}$$

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial}{\partial \beta} \left(\frac{\partial Z}{\partial \beta} \right)$$

$$= \frac{1}{Z} \frac{\partial}{\partial \beta} \left(-Z \langle E \rangle \right)$$

$$= -\frac{1}{Z} \left\{ \frac{\partial \langle E \rangle}{\partial \beta} \cdot Z + \langle E \rangle \frac{\partial Z}{\partial \beta} \right\}$$

$$= -\frac{\partial \langle E \rangle}{\partial \beta} + \langle E \rangle \frac{1}{Z} \cdot Z \langle E \rangle$$

$$\langle E^2 \rangle = \frac{-\partial \langle E \rangle}{\partial \beta} + \langle E \rangle^2$$

$$\langle E^2 \rangle - (\langle E \rangle)^2 = -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$= -\frac{\partial T}{\partial \beta} \cdot \frac{\partial \langle E \rangle}{\partial T}$$

But $\dfrac{\partial T}{\partial \beta} = \left(\dfrac{\partial \beta}{\partial T}\right)^{-1} = \left[\dfrac{\partial (kT)^{-1}}{\partial T}\right]^{-1}$

$$= \left(\frac{-1}{kT^2}\right)^{-1} = -kT^2$$

AND $\dfrac{\partial \langle E \rangle}{\partial T}$ = Heat Capacity C_V.

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 C_V$$

$$\sigma_E^2 = kT^2 C_V$$

$$\sigma_E = kT \sqrt{\frac{C_V}{k}}$$

Already showed (P92 of text)

$$C_V = \frac{\partial}{\partial T}(NkT) = Nk$$

So $\sigma_E \sim \sqrt{N}$

Also $\frac{\langle E \rangle}{N} = \frac{\hbar\omega}{e^{\cdots} - 1} \rightarrow \langle E \rangle \sim N$

So $\frac{\sigma_E}{E} \sim \frac{1}{\sqrt{N}}$

as $N \rightarrow \infty$ fluctuations around average $\rightarrow 0$.

So $\langle E \rangle$ is observed value of E.

Z determines $F \rightarrow$ All of ThermoDynamic Properties

$$F = E - TS \longrightarrow \text{fn of } T, V, N$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{VN} dT + \left(\frac{\partial F}{\partial V}\right)_{TN} dV + \left(\frac{\partial F}{\partial N}\right)_{TV} dN$$

$$= -S\,dT \quad - p\,dV \quad + \quad \mu\,dN$$

want to show $F = -kT \ln Z(T, V, N)$

define $\tilde{F} = -kT \ln Z$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{NV} = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z \quad ①$$

and for large N $\langle E \rangle \rightarrow E$

already showed $\dfrac{\partial}{\partial T} \ln Z = \dfrac{\langle E \rangle}{kT^2}$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{NV} = -k \ln Z - kT \frac{E}{kT^2}$$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{NV} = -k \ln Z - \frac{E}{T}$$

defined $\tilde{F} = -kT \ln Z$

so $$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{NV} = \frac{\tilde{F} - E}{T} \quad (2)$$

and $$\left(\frac{\partial F}{\partial T}\right)_{NV} = -S \quad ; \quad F = E - TS$$

so $$= \frac{F - E}{T} \quad (3)$$

(2) and (3) mean F & $\tilde{F}$ obey same 1st order differential equation

If they agree at some Boundary Con. then F & $\tilde{F}$ are same function.

$$\tilde{F} = -kT \ln Z =$$

$$= -kT \ln e^{-E_0/kT}\left(1 + \underbrace{e^{-(E_1-E_0)/kT}}_{\to 0}\right)$$

AS $T \to 0$ $\tilde{F} \to E_0$

$$\left(\to -kT \ln e^{-E_0/kT} = -\frac{kT}{kT} E_0 = E_0 \right)$$

$E_0 \to$ Ground STATE ENERGY

F? $F = E - TS$

as $T \to 0$ $F \to E$ $\to$ tends to MINIMUM

So $E \to E_0$

$$\left.\begin{aligned} \tilde{F}\big|_{T=0} &= E_0 \\ F\big|_{T=0} &= E_0 \end{aligned}\right\} F \equiv \tilde{F}$$

So $F = -kT \ln Z$

SUMMARY — CANONICAL ENSEMBLE

$$Z(T,V,N) = \sum_{\underset{\mu\text{states}}{s}} e^{-E_s/kT}.$$

$$F(T,V,N) = -kT \ln Z(T,V,N)$$

$$p = \left(\frac{-\partial F}{\partial V}\right)_{TN}$$

$$S = \left(\frac{-\partial F}{\partial T}\right)_{NV}$$

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

Complete thermo Dynamic Description of SYSTEM