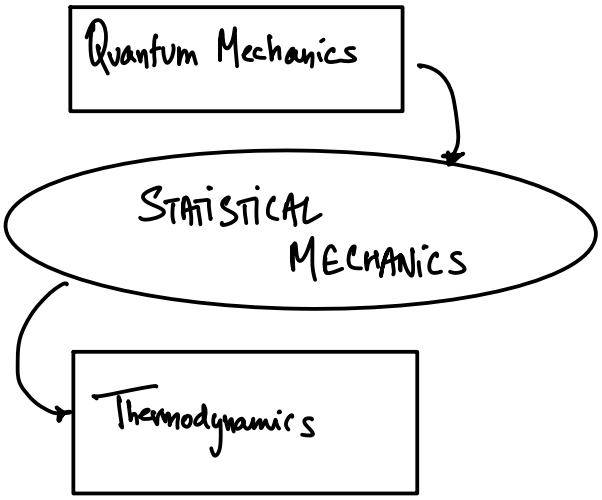
STATISTICAL MECHANICS:



for (eg)

thermodynamics tells us → thermal expansion.

$$C_p - C_V = T V \beta^2 / \underline{K}$$ → compressibility

relates these quantities but does not tell us how to calculate any of them.

① Coarse-graining

* macroscopic thermodynamics ⟶ few variables. ⟵ Stat mech will tell us how to "Simplify"
* atomistic scale ⟶ many variables ~ 10^{23}

②

STATIC v/s DYNAMIC:

Thermo ⟶ eqm state is static

Microscopic / Atomic level ⟶ a system is fluctuating

How do we relate eqm thermodynamic quantities to fluctuating microscopic quantities?

③ What is entropy, internal energy etc. ... ?

BASIC IDEAS BEHIND STAT MECH:

— Mechanical variables $[H, X_i, \cdots]$ are time averages.

$$H = \langle E \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t E(\tau)\, d\tau$$

— What is needed?

① How do I do the averaging?

In principle for time averages:

- dynamics (equations of motion)
- how atoms interact
- ∞ time!!

very HARD $\Longrightarrow$ POSTULATE (I) OF STAT MECH

time average = weighted average over all possible states

$$U = \langle E \rangle = \lim_{t\to\infty} \frac{1}{t}\int_0^t E(z)\,dz = \int E(\vec{r},\vec{p})\, P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p}$$

Consider N particles:

each particle has a position $\vec{r}_i = (r_{ix}, r_{iy}, r_{iz})$

momentum $\vec{p}_i = (p_{ix}, p_{iy}, p_{iz})$

The entire system can then be characterized by 2 vector of dimension 3N

$$\vec{r} = (r_{1x}, r_{1y}, \cdots, r_{Nz})$$

$$\vec{p} = (p_{1x}, p_{1y}, \cdots, p_{Nz})$$

$P(\vec{r},\vec{p})$ = probability density

P is "large" in regions of $\vec{p},\vec{r}$ that are likely and small in regions that are unlikely.

$P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p}$ $\longrightarrow$ measure of time that the system spends in a state between $[(\vec{r},\vec{p}) : (\vec{r}+d\vec{r}, \vec{p}+d\vec{p})]$

$$\langle E \rangle = \int E(\vec{r},\vec{p})\, P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p} \longrightarrow \text{"ENSEMBLE" average.}$$

"ENSEMBLE" $\longrightarrow$ all possible microscopic states of the system

② Probability that a system occupies a give state

③ Which states to average over?

$\longrightarrow$ Eigen states of a system $\leftarrow$ formally from QM.

④ Relate to thermo quantities

* Which states to average over?

$\hat{H}\Psi = E\Psi$ → Solve Schrödingers equation at fixed $N, V, \dots$

- notice "T" → temperature is not a variable in this equation

* SOLUTIONS:

Spectrum of eigenvalues

E_ν quantized → $\vdots$, E_2, E_1, lowest → E_0 energy "ground" state

for each energy → many eigenstates

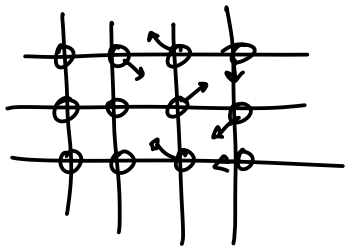
$\vdots$

$\Psi_{01}, \Psi_{02}, \dots, \Psi_{0\Omega(E_0)}$ — degeneracy

* for the purposes of Stat. mech → we view the system as fluctuating from one eigenstate to the next

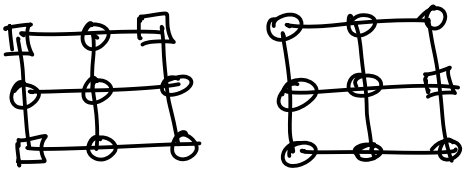
EXAMPLES OF MICROSTATES (for solids):

* vibrational microstates



atom vibrate around their eq^m sites

* configurational microstates



- each state corresponds to a microstate
- each state has a well-defined energy.

□ → A

○ → B

* CIRCLING BACK TO STATISTICAL MECHANICS:

POSTULATE I: The time average of a mechanical variable is equal to its ensemble average

M → mechanical variable → ($\overset{u}{E}$, b, V, N, ...)

$$\overline{M} = \lim_{t\to\infty} \frac{1}{t}\int_0^t M(t)\,dt = \sum_\nu M(\nu)\,\mathcal{P}(\nu)$$

example $U = \overline{E} = \sum_\nu E_\nu \mathcal{P}_\nu$

Pressure: $p \longrightarrow$ what is the microscopic counterpart?

- microstate $\eta \longrightarrow E_\eta(N,V)$ $\quad dE_\eta(N,V) = \frac{\partial E_\eta}{\partial V} dV = -p_\eta dV$ (p_η: pressure of microstate η)

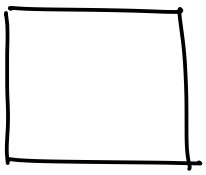
$$\bar{p} = \langle p \rangle = \sum_\eta p_\eta P_\eta = \sum_\eta \left(-\frac{\partial E_\eta}{\partial V}\right) P_\eta$$

★ How do we calculate $P_\nu \longrightarrow$ probability of a microstate

P_ν depends on the boundary conditions applied to the system

① MICROCANONICAL ENSEMBLE (constant N, V, E) $\longrightarrow$ isolated adiabatic

fixed $E \Rightarrow$ system can only fluctuate between states with the same energy E



$N, V \rightsquigarrow H\Psi = E\Psi \longrightarrow$ find all eigenstates with energy E $\quad \{\Psi_1, \Psi_2, \dots, \Psi_\Omega\}$

$\Omega(E) \rightarrow$ # of microstates with energy E

POSTULATE:

$$P_\nu = \text{constant} = \frac{1}{\Omega(E)} \Rightarrow \sum_\nu P_\nu(E) = 1$$

also called Principle of a-priori probabilities

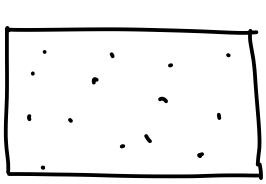
$$\bar{M} = \sum_\nu M_\nu P_\nu = \frac{1}{\Omega} \sum_\nu M_\nu$$

IMPLICATIONS:

The macroscopically observed state will be the one with the most microstates.

(eg) non-interacting gas:

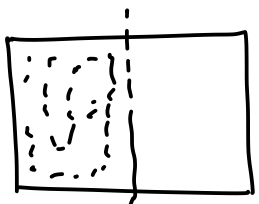
(A)



macrostate $\longrightarrow$ "homogeneous"

↑ MORE MICROSCOPIC STATES

(B)



macrostate $\longrightarrow$ "all atoms are in one half of the box"

Notice $\longrightarrow$ microstates for both (A) & (B) have the same probabilities.

$P_A = \sum_{\nu} P_\nu$ $\qquad$ $P_B = \sum_{\theta}$ P_θ

$\theta \in$ atoms are in only ½ the box

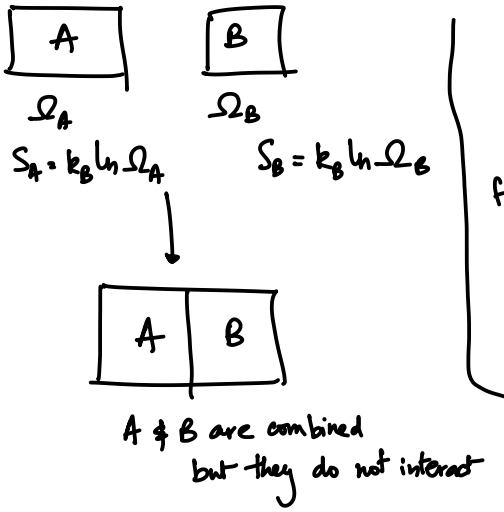
$P_A \gg P_B$

→ What is entropy?

$S = k_B \ln \Omega(E, V, N)$ ← Boltzmann.

Ω ← # of microstates with E, V, N

why is it logarithmic?



A & B are combined but they do not interact

$\Omega_{A+B} = \Omega_A \times \Omega_B$ ← # of microstates for the A & B systems.

S → extensive ← product] related

from thermo $S_{A+B} = S_A + S_B$ ← sum

HAS TO BE logarithmic

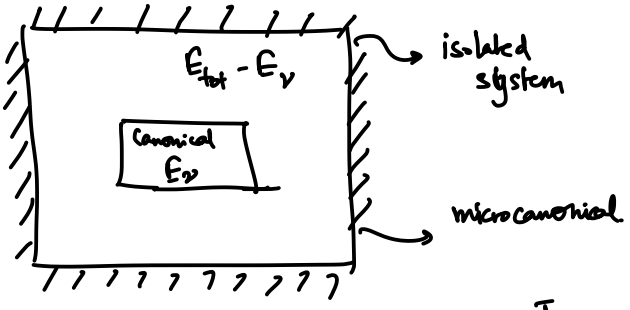
$\Rightarrow$ $S_A = k_B \ln \Omega_A$, $S_B = k_B \ln \Omega_B$]

$S_{A+B} = k_B \ln(\Omega_A \Omega_B)$

$= k_B \ln \Omega_A + k_B \ln \Omega_B = S_A + S_B$

② Canonical Ensemble [constant N, V, T]

→ P_ν in the canonical ensemble (from Chandler)



Starting from the microcanonical ensemble, it can be shown that

$$P_\nu \propto \exp\left(-E_\nu / k_B T\right) = \exp\left(-\beta E_\nu\right) \qquad \beta = 1/k_B T$$

$$\sum_\nu P_\nu = 1$$

$$\Rightarrow \boxed{P_\nu = \frac{\exp(-\beta E_\nu)}{\sum_\lambda \exp(-\beta E_\lambda)}}$$

Q: Z = partition function

$$\boxed{Z = \sum_\nu \exp\left(-\beta E_\nu\right)}$$

★ A closer look at probabilities:

$$P_\nu = \frac{\exp\left(-\beta \Delta E_\nu\right)}{\sum_\lambda \exp\left(-\beta\left(\Delta E_\lambda\right)\right)} = \frac{\exp\left(-\beta\left(E_\nu - E_0\right)\right)}{\sum_\lambda \exp\left(-\beta\left(E_\lambda - E_0\right)\right)} = \frac{\exp\left(-\beta E_\nu\right)\exp\left(+\beta E_0\right)}{\left[\sum_\lambda \exp\left(-\beta E_\lambda\right)\right]\exp\left(+\beta E_0\right)}$$

(I) $T \to 0 \quad \beta \to \infty$

$$\lim_{T\to 0} P_\nu = \begin{cases} \frac{1}{\Omega(E_0)}, & \text{if } E(\nu) = E_0 \\ 0, & \text{otherwise} \end{cases}$$

→ only "groundstate" is occupied

(II) $T \to \infty \quad (\beta \to 0)$

$\exp\left(-\beta \Delta E_i\right) \to 1$ for all states.

P_ν is constant ⇒ every microstate has equal probability.

Relating Statistical Mechanics to Macroscopic Thermodynamics

$$\boxed{F = -k_B T \log Z} \qquad F(N,V,T) = U - TS \rightarrow$$ this is the relevant char. potential @ the macroscale.

★ ENTROPY IN THE GIBBS FORMULA:

$$S = -k_B \sum_i P_i \log P_i$$

proof: $P_i = \frac{\exp(-\beta E_i)}{Z}$

$$\sum_i P_i \log P_i = \sum_i \frac{\exp(-\beta E_i)}{Z} \left[-\beta E_i - \log Z\right]$$

$$= -\beta \sum_i P_i E_i - \log Z \underbrace{\sum_i \frac{\exp(-\beta E_i)}{Z}}_{1}$$

$$\boxed{\sum_i P_i \log P_i = -\beta \bar{E} - \log Z}$$

$$-\log Z = \beta F$$

$$\Rightarrow -\beta(F - \bar{E}) = -\frac{S}{k_B}$$

- Interpretation:

(I) In the microcanonical ensemble: $P_i = \frac{1}{\Omega}$; $E_i = \text{constant} = E$

$$S = -k_B \sum_i P_i \log P_i = -k_B \sum_i P_i \log\left(\frac{1}{\Omega}\right) = k_B \sum_i P_i \log \Omega$$

$$\Rightarrow \boxed{S = k_B \log \Omega} \Longrightarrow \text{we recover Boltzmann.}$$

(II) $S = -k_B \sum_i P_i \log P_i$

↑ "averaging" this quantity over all microstates.

There is no microscopic entropy to average over

$\Rightarrow$ S is a property of the distribution itself.

Notice: S does not look like

$$\left[\bar{V} = \langle V \rangle = \sum_\nu P_\nu V_\nu \right]$$

$$\left[\bar{E} = \langle E \rangle = \sum_\nu P_\nu E_\nu \right]$$

(III) S does not depend on the energy reference

Say the system has some energy levels $\rightarrow E_i$

Let us shift these energy scales: $E_i' = E_i + \Delta E$; ↳ constant shift of energy.

$$\boxed{S' = \sum_i P_i' \log P_i' = S} \longrightarrow S \text{ is invariant under change of the energy reference.}$$

(IV) S @ the extremes of temperature:

$$P_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(E_i \beta)}$$

lowest state E_0

$E_0 < E_1 < E_2 < \cdots$

$$P_0 = \frac{\exp(-\beta E_0)}{\exp(-\beta E_0)\left[1 + \sum_{j=1}^{\infty} \exp(-\beta(E_j - E_0))\right]} = \frac{1}{1 + \sum_{j=1}^{\infty} \exp(-\beta(E_j - E_0))}$$

$T \rightarrow 0 \quad \beta \rightarrow \infty$

$\Rightarrow \boxed{P_0 = 1}$

at zero T: if $E_i = E_0$; $P_i = 1$

else $P_i = 0$

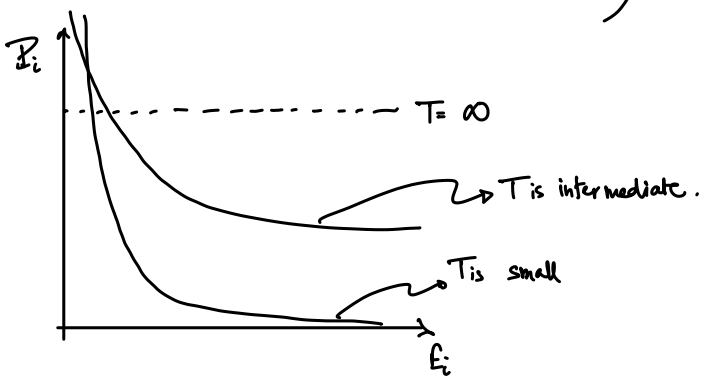
Entropy: $S = -k_B \sum_i P_i \log P_i = -k_B \left[1 \log 1 + 0 \log 0 + \cdots \right]$

↑ L'Hospital's rule to show $\lim_{x \to 0} x \log x = 0$

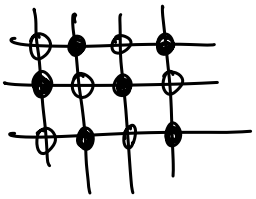
$\boxed{S = 0}$ → ABSOLUTE REFERENCE FOR ENTROPY @ $T = 0$ $\Rightarrow$ III Law of thermodynamics.

$T \to \infty \quad \beta \to 0$

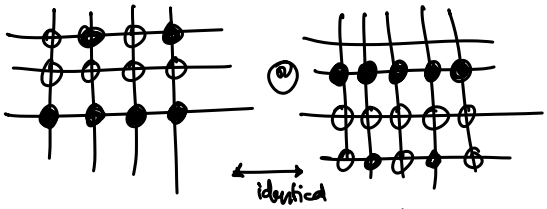
P_i = constant $\left(\because \exp(-\beta E_i)/Z = 1/Z \right)$



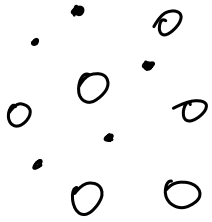
EXAMPLE: A-B alloy bond energies: $\phi_{AB} < \phi_{AA}, \phi_{BB}$



E = low



E = intermediate



E = high

liquid-like, many many possibilities

low T: probability of ordered state much higher than that of the other states.
system mostly resides in ordered state

intermediate T: P_i of "disordered" or higher energy states becomes significant. Many more disordered states than ordered states.
On average we don't see the ordered state

high T: $\Omega(E_{liquid}) >>> \Omega(E_{solid})$