

Boltzmann's Formula

$$S = k_B \ln \Omega$$

$$k_B = R/N_A = 1.38 \cdot 10^{-23} \text{ J/K}$$

Ω : number of microstates in a system

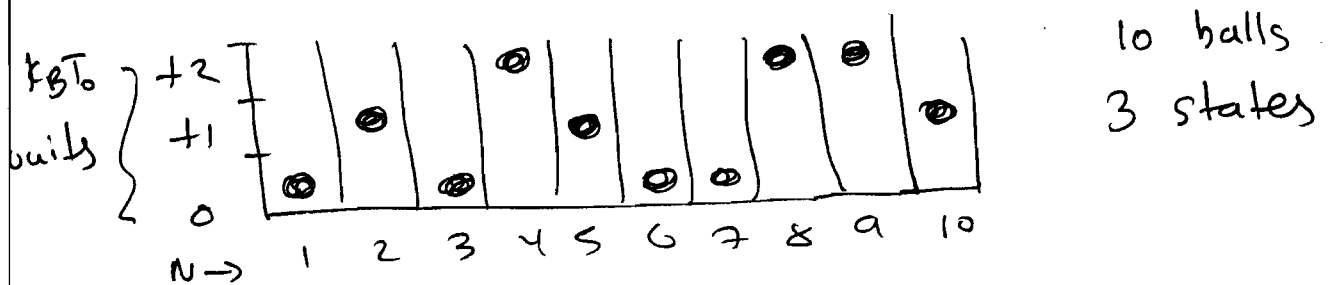
• natural in quantum mechanics, where only discrete states are populated

• in classical, continuum systems one needs to set a parameter for how different two states need to be to count as separate -

$$\text{e.g. } \sum_{i=1}^N |\vec{r}_{i\alpha} - \vec{r}_{i\beta}| < \delta \Rightarrow \alpha \equiv \beta$$

If δ changes, S gets shifted by a constant; classical S is only defined after setting an (arbitrary) reference

• easy to obtain in classical discrete systems (e.g., lattice models)



$$U=0 \quad \Omega=1 \quad S=0 \quad (\text{ground state})$$

$$U=1 \quad \Omega=10$$

$$U=2 \quad \Omega = 10 + \binom{10}{2} = 10 + \frac{10 \cdot 9}{1 \cdot 2} = 55$$

...

Correspondence with "classical" S

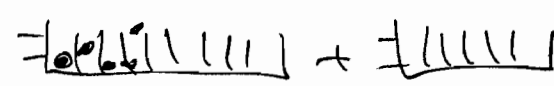
$\Delta S = \frac{Q^{rev}}{T}$ in classical thermodynamics, nothing to do with microstates

"Statistical" $S = k_B \ln \Omega$ has 2 key properties:

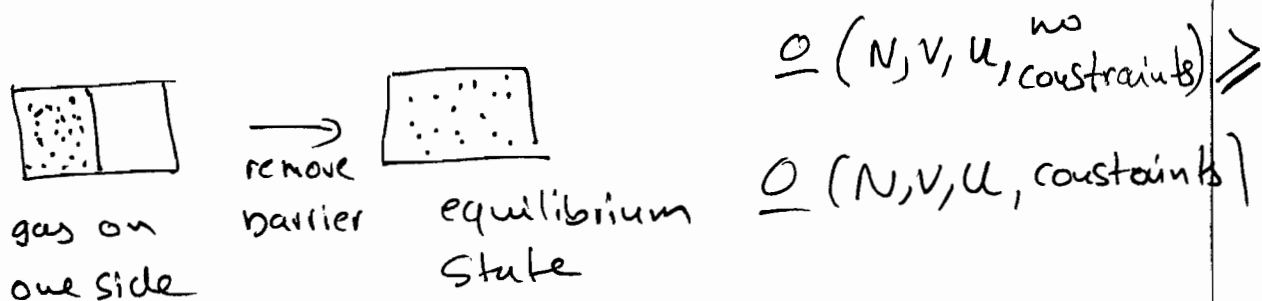
① S is extensive

For two independent subsystems A + B

$$S_{A+B} = k_B \ln(\Omega_{A+B}) = k_B \ln(\Omega_A \cdot \Omega_B) = S_A + S_B$$

e.g.  two ^{identical} boxes

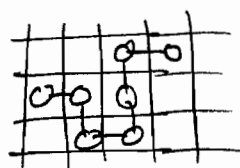
② S is maximized at equilibrium



Since removal of constraints always makes new microstates available

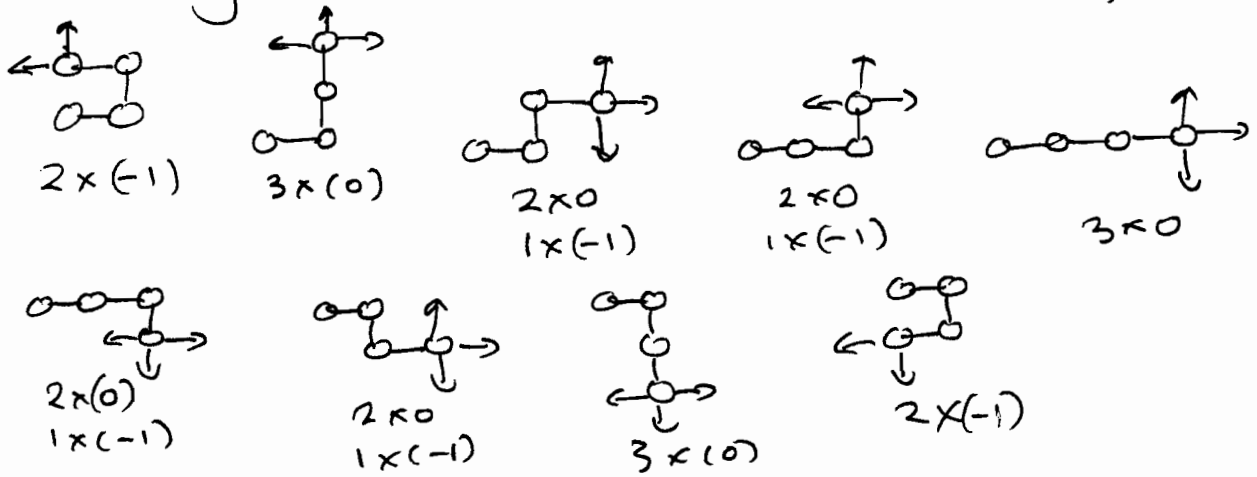
Example 1 Entropy of a lattice chain (distinct conformers)

A simple model for polymers: Flory lattice model



- each bead occupies a lattice site
- volume exclusion (no double-occupancy)
- non-bonded nearest-neighbor interactions worth -1 units of u (one such contact in) $[-k_B T_0]$

Counting microstates for $m=5$ beads, 2D



$$\underline{\Omega}(u=0) = 3 + 2 + 2 + 3 + 2 + 2 + 3 = 17 \quad \underline{\Omega}(u=1) = 8$$

Phase Space and Stat. Mech. Ensembles

Statistical Mechanics links microscopic variables (3N positions, 3N velocities of atoms in a system)

to macroscopic properties (e.g. pressure, energy)

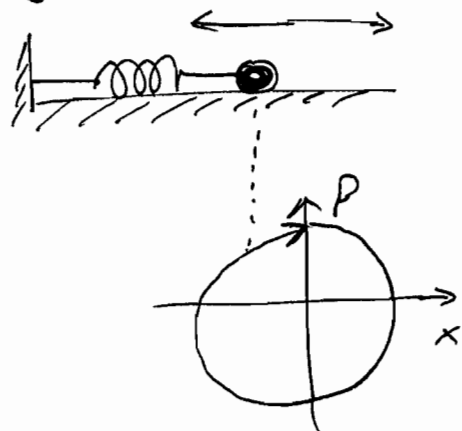
Phase Space multidimensional space of microscopic variables

$$(\vec{r}^N, \vec{p}^N) = (\underbrace{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N}_{\text{positions}}, \underbrace{\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N}_{\text{momenta}} \quad \vec{p}_i = m_i \vec{v}_i)$$

For classical systems, Newton's equations describe evolution in phase space:

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i \quad ; \quad m \frac{d\vec{v}_i}{dt} = - \frac{\partial U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{\partial \vec{r}_i}$$

E.g., for a one-dimensional harmonic oscillator



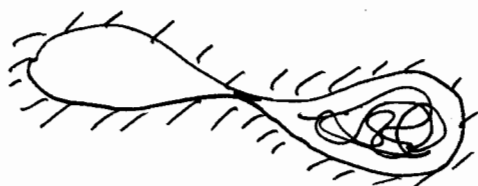
trajectory is a circle in 2-d phase space (after scaling of p and x)
 Circle radius depends on total energy (constant)

A Statistical Mechanical Ensemble is a set of microstates consistent with a set of macroscopic constraints (e.g. const. U, V, N).

Systems can be described by equilibrium Stat. Mech. only if they obey the "ergodic hypothesis":

For sufficiently long times, such systems explore all microscopic states consistent w/ ext. + int. constraints

→ equivalent to classical postulate on existence of stable equilibrium states.



non-ergodic system
 (e.g. a glass)

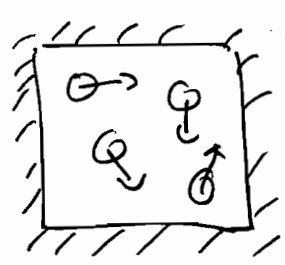


ergodic system

$$F_{\text{observed}} = \underbrace{\sum_{\text{all microstates}} P_v \cdot F_v}_{\text{ensemble average}} = \langle F \rangle$$

(time average)

Microcanonical Ensemble: const U, V, N



- isolated system in rigid container
- follows Newton's equations (classically)

Basic Postulate of Stat. Mech. :

at const. U, V, N all microstates are equally probable

$$P_v = \frac{1}{\Omega(U, V, N)} \quad \left| \begin{array}{l} \text{Probability of each} \\ \text{microstate} \end{array} \right.$$

Fundamental Equation of Stat. Mech.

$$dU = T dS - P dV + \mu dN \quad (\text{1-comp., classical f. } \epsilon)$$

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

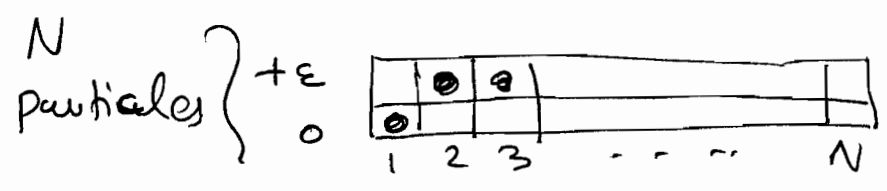
$$d \ln \Omega = \frac{1}{k_B T} dU + \frac{P}{k_B T} dV - \frac{\mu}{k_B T} dN \quad (1)$$

$\frac{1}{k_B T} \equiv \beta$ Standard notation in Stat. Mech.

Differential relationships of (1):

$$\beta = \left. \frac{\partial \ln \Omega}{\partial U} \right)_{V, N} ; \quad \beta P = \left. \frac{\partial \ln \Omega}{\partial V} \right)_{U, N} ; \quad -\beta \mu = \left. \frac{\partial \ln \Omega}{\partial N} \right)_{U, V}$$

Example



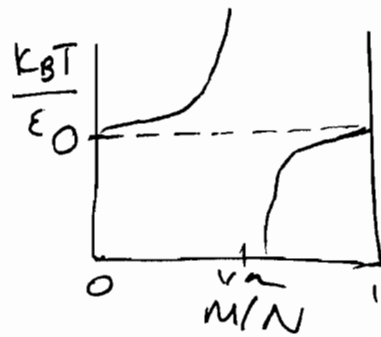
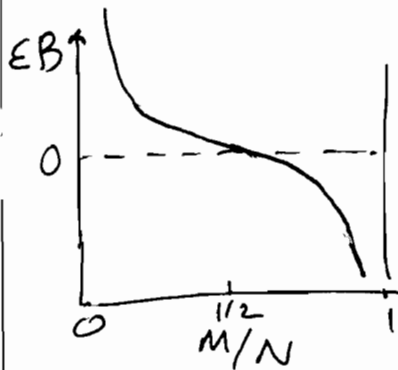
$\left. \begin{array}{l} \text{fixed positions} \\ \text{energy} \end{array} \right\} \begin{array}{l} 0 \text{ or} \\ \text{levels} \end{array} \left. \begin{array}{l} +3 \\ M \text{ at } +\epsilon \end{array} \right)$

$$\underline{\Omega}(u) = \binom{N}{M} = \frac{N!}{M!(N-M)!} \left[\begin{array}{l} \text{for } N \rightarrow \infty \\ \ln N! \approx N \ln N - N \end{array} \right]$$

$$\ln \underline{\Omega} = N \ln N - M \ln M - (N-M) \ln(N-M) - N + M + (N-M) - N + M$$

$$\left[B = \frac{\partial \ln \underline{\Omega}}{\partial u}, \quad u = M \epsilon \right] \Rightarrow \epsilon B = \frac{\partial \ln \underline{\Omega}}{\partial M} =$$

$$= -\ln M + \ln(N-M) + 1 \Rightarrow \epsilon B = \ln \frac{N-M}{M}$$



$$\Rightarrow \frac{k_B T}{\epsilon} = \frac{1}{\ln \left(\frac{N}{M} - 1 \right)}$$

Negative temperatures exist in systems with energies that "saturate" - e.g., spin systems, polymers

"Normal" systems (e.g. gases in a container) do not have limits to u , $T > 0$ always

B is a more natural measure of temperature.

Shows that $T \rightarrow 0$ is infinitely far away,

Proximity of $+\infty$ and $-\infty$