Statistical Mechanics

sampling + averaging

microscopic $\longrightarrow$ **macroscopic**

Newton's eq.
or
Schrodinger's eq.

Thermodynamics

Basic idea

given enough time – system will explore all microscopic states consistent with constraints

$$G_{obs} = \frac{1}{N}\sum_{a=1}^{N} G_a$$

instantaneous measurements (of course in a real experiment measurements have a time duration)

- But # of energetically accessible microstates can be astronomical.
- In computer simulations – need to sample

$$\langle G \rangle = G_{obs} = \sum_{v} P_v G_v, \qquad G_v = \langle v | G | v \rangle$$

ensemble averaged

probability of being in state *v*

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microcanonical ensemble
all states with fixed *E, N, V*

closed isolated system

canonical ensemble
all states of fixed *N, V*
E can fluctuate

closed system in contact with heat bath

(sometimes called NVT)

Ergodic Systems

time average = ensemble average

Isolated system: All microstates (of a given energy) are equally probable

$\Rightarrow$ Macroscopic equil. state corresponds to the most random situation

$\Omega(N,V,E) =$ # states with *N, V,* and energy between *E* and $E + \delta E$

relatively insensitive to δE

due to limitations in our ability to specify *E*

$\bar{\Omega}(N,V,E)\,dE =$ # of states with energy between *E* and $E + dE$

density of states
(in continuum limit)

$$P_\nu = \frac{1}{\Omega(N,V,E)} =$$ probability of macroscopic state ν

$S = k_B \ell n\ \Omega$ ⟵ **definition of Entropy**

$\left(k_B = 1.38x10^{-16} erg / \deg\right)$

consider two subsystems, A and B ⟶

A	B
Ω_A	Ω_B

total # states = $\Omega_A \Omega_B$

$$S = k_B \ell n\left[\Omega_A \Omega_B\right] = k_B \ell n \Omega_A + k_B \ell n \Omega_B$$

$$= S_A + S_B$$ ⟵ additive as it should be

A	B	→	A + B
N_A	N_B		$N_A + N_B$
V_A	V_B		$V_A + V_B$
E_A	E_B		$E_A + E_B$

$\Omega_A \Omega_B < \Omega_{A+B}$

$S_A + S_B (constr.) < S_{A+B}$

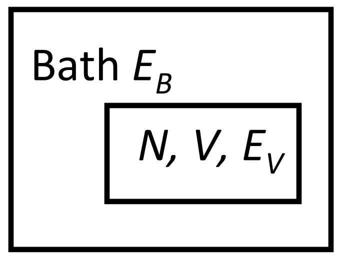
system evolves toward more disorder

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$ definition

$$\Rightarrow \beta = \frac{1}{k_B T} = \left(\frac{\partial \ell n \Omega}{\partial E}\right)_{N,V}$$

T is positive $\Rightarrow \Omega$ monotonically increases with E

Canonical ensemble: *N, V*
heat bath at temp T



Energy can flow between
E_B and E_V

Entire system – subsystem and bath is microcanonical, i.e., *N, V, E*

Assume $E_B >> E_V$
bath so large, its energy levels are continuous

If sub-system in state E_V, $\boxed{E = E_B + E_v = \text{fixed}}$

probability of observing system in state $v \propto$ *# states with energy E-E_v*

$$P_v \propto \Omega\left(E - E_v\right) = e^{\ell n\left[\Omega\left(E - E_v\right)\right]}$$

$$P_v = \Omega_B\left(E - E_v\right) / \Omega_{tot}\left(E\right)$$

$$\ell n\Omega\left(E - E_v\right) = \ell n\Omega\left(E\right) - E_v \underbrace{\frac{d\,\ell n\Omega\left(E\right)}{dE}}_{\beta} + \ldots$$

Taylor series,
assuming E_v << E

$$P_v \propto e^{-\beta E_v} \quad \longleftarrow$$ **Boltzmann distribution**

$$\sum_v P_v = 1$$

To determine
proportionality const.

$$P_v = \frac{e^{-\beta E_v}}{Q}, \qquad Q = \sum_v e^{-\beta E_v} =$$ canonical partition function

$$\langle E\rangle = \Sigma P_v E_v = \frac{\Sigma E_v e^{-\beta E_v}}{\Sigma e^{-\beta E_v}} = \frac{\left[-\partial Q/\partial\beta\right]_{N,V}}{Q} = -\left(\frac{\partial \ell n Q}{\partial\beta}\right)_{N,V}$$

$$A = -\frac{1}{\beta}\ell n Q$$

Assume for now

$$S = \frac{\langle E\rangle}{T} + k\ell n \mathrm{Q} + const$$

can ignore

$$\langle P\rangle = \frac{1}{\beta}\left(\frac{\partial \ell n Q}{\partial V}\right)_{N,T}$$

$$Q = \sum_v e^{-\beta E_v} = \sum_v \langle v|e^{-\beta H}|v\rangle = Tr\left[e^{-\beta H}\right]$$

Trace is independent of representation
Don't have to solve Schrodinger Eq.

For macroscopic systems, in general, properties do not depend on ensemble

$$Q = \sum_v e^{-\beta E_v} = \sum_l \Omega(E_l)e^{-\beta E_l}$$

Switch from sum over states to over energy levels

$$Q = \int_0^\infty e^{-\beta E}\bar{\Omega}(E)\,dE$$

canonical partition funct.

microcanonical

Laplace transform
holds for large systems

Energy of system fluctuates in canonical ensemble

$$\left\langle(\delta E)^2\right\rangle=\left\langle\left(E-\langle E\rangle\right)^2\right\rangle=\left\langle E^2\right\rangle-\langle E\rangle^2$$

$$=\Sigma P_v E_v^2-\left(\Sigma P_v E_v\right)^2$$

$$=\frac{1}{Q}\left(\frac{\partial^2 Q}{\partial\beta^2}\right)_{N,V}-\frac{1}{Q^2}\left(\frac{\partial Q}{\partial\beta}\right)_{N,V}^2$$

$$=\left[\frac{\partial^2}{\partial\beta^2}\ell nQ\right]_{N,V}=-\left[\frac{\partial\langle E\rangle}{\partial\beta}\right]_{N,V}$$

$$\langle E\rangle=-\left(\frac{\partial\ell nQ}{\partial\beta}\right)_{N,V}$$

$$\left\langle(\delta E)^2\right\rangle=k_B T^2 C_V$$

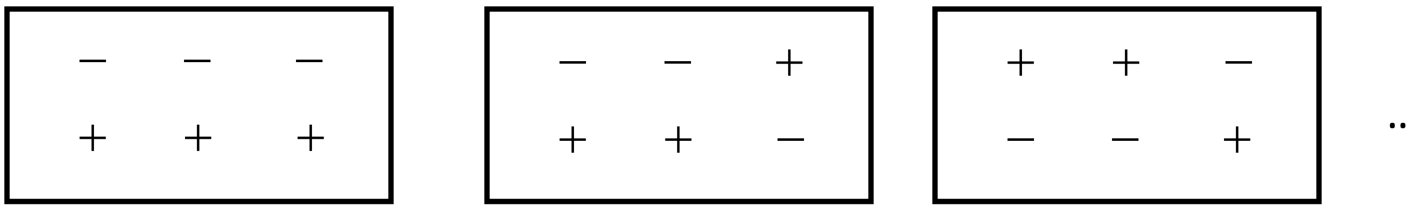
$$\frac{\sqrt{\left\langle\left[E-\langle E\rangle\right]^2\right\rangle}}{\langle E\rangle}=\frac{\sqrt{k_\beta T^2 C_V}}{\langle E\rangle}\sim\vartheta\left(\frac{1}{\sqrt{N}}\right)$$

for $N \sim 10^{23}$,
fluctuations
are tiny portion
of total energy

A simple example

Collection of N non-interacting 2-level (E = 0 or ε) distinguishable particles

$$\nu = (n_1, \dots, n_N),\; n_j = 0 \text{ or } 1 \quad \text{Defines a state with energy } \sum_{j=1}^{N} n_j \varepsilon$$



0 ε 2ε

$$\Omega(E,N) = \frac{N!}{(N-m)!\,m!}, \quad E = m\varepsilon$$

$$\frac{S}{k_B} = \ell n\,\Omega(E,N)$$

$$\beta = \frac{1}{k_B}\left(\frac{\partial \ell n \Omega}{\partial E}\right)_N = \frac{1}{\varepsilon}\left(\frac{\partial \ell n \Omega}{\partial m}\right)_N$$

Chose m objects from N objects

Consider 3 particles

E = 0, 1 way

E = 1ε, 3 ways,

E = 2ε, 3 ways

$$\ell n\,(M!) \approx M\,\ell n M - M$$ (Stirling's approximation)

$$\frac{\partial \ell n \Omega}{\partial m} = \ell n\left(\frac{N}{m} - 1\right) = \beta \varepsilon$$

$$\frac{m}{N} = \frac{1}{1 + e^{\beta\varepsilon}}$$

$$\frac{N}{m} - 1 = e^{\beta\varepsilon}$$

$$\frac{N}{m} = 1 + e^{\beta\varepsilon}$$

$$E = m\varepsilon, \qquad m = E/\varepsilon$$

$$\frac{E/\varepsilon}{N} = \frac{1}{1 + e^{\beta\varepsilon}}$$

$$E = N\varepsilon \frac{1}{1 + e^{\beta\varepsilon}} \rightarrow \begin{cases} 0, & T \to 0 \\ \dfrac{N\varepsilon}{2}, & T \to \infty \end{cases}$$

get exactly same result for
<*E*> in canonical ensemble

Other ensembles

changes in ensembles $\leftrightarrow$ Legendre transforms of S

Let $S = k_B \ell n \Omega(E, X)$

mechanical extensive variables

$$\frac{1}{k_B} dS = \beta dE + \xi dX$$

if $\begin{cases} X = N, & \xi = -\beta\mu \\ X = V, & \xi = \beta p \end{cases}$

etc.

$$\boxed{dS = \frac{1}{T} dE - \frac{f}{T} \cdot dX}$$

from chpt. 1

$$\frac{1}{k_B} dS = \beta dE - \beta f \cdot dX$$

Be careful about Chandler's sign convention here

Suppose both *E* and *X* can fluctuate

$$P_v = \frac{e^{-[\beta E_v + \xi X_v]}}{\Xi}, \qquad \Xi = \Sigma e^{-(\beta E_v + \xi X_v)}$$

$$\langle E \rangle = \Sigma P_v E_v = \left[\frac{\partial}{\partial(-\beta)} \ell n \Xi \right]_{\xi, Y}$$

$$\langle X \rangle = \Sigma P_v X_v = \left[\frac{\partial}{\partial(-\xi)} \ell n \Xi \right]_{\beta, Y}$$

$$S = -k_B \sum_v P_v \ell n P_v$$

Gibbs Entropy Equation

Quick check. For simplicity assume canonical ensemble. Plug in expression for P_v – can show that

$S = \frac{< E >}{T} + k \ell n Q$ which we showed previously.

Grand Canonical Ensemble

E and *N* can fluctuate

$$P_\nu = \Xi^{-1} e^{-\left(\beta E_\nu - \beta\mu N_\nu\right)}$$

$$S = -k_B \sum_\nu P_\nu \left[-\ell n \Xi - \beta E_\nu + \beta\mu N_\nu\right]$$

$$= -k_B \left[-\ell n \Xi - \beta \langle E \rangle + \beta\mu \langle N \rangle\right]$$

$$\ell n \Xi = \frac{S}{k_B} - \beta \langle E \rangle + \beta\mu \langle N \rangle$$

$$\ell n \Xi = \beta p V$$

using $E - TS + pV = \mu n$ from p 24

$$\left(\frac{\partial \langle N \rangle}{\partial \beta\mu}\right)_{\beta,V} = \left\langle \left(\delta N\right)^2 \right\rangle \geq 0$$

$$-\frac{\partial \langle E \rangle}{\partial \beta} = \left\langle \left(\delta E\right)^2 \right\rangle = k_B T^2 C_\nu \geq 0$$

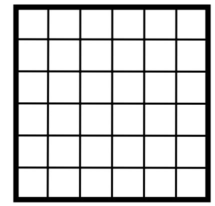
$$-\frac{\partial \langle X \rangle}{\delta \xi} = \left\langle \left(\delta X\right)^2 \right\rangle \geq 0$$

$$\left\langle \left(\delta N\right)^2 \right\rangle = \left\langle N^2 \right\rangle - \left\langle N \right\rangle^2$$

$$= \Sigma P_\nu N_\nu^2 - \left(\Sigma P_\nu N_\nu\right)^2$$

Non-interacting particles

$$\left\langle (\delta N)^2 \right\rangle = \left\langle N^2 \right\rangle - \left\langle N \right\rangle^2$$
$$= \sum_{i,j} \left[\left\langle n_i n_j \right\rangle - \left\langle n_i \right\rangle \left\langle n_j \right\rangle \right]$$



occupation of cell *i*

$$n_i = 0 \text{ or } 1$$
$$N = \sum_{i=1}^{m} n_i$$

Assume occupations of cells are uncorrelated, and average occupations are low

if uncorrelated $\left\langle n_i n_j \right\rangle = \left\langle n_i \right\rangle \left\langle n_j \right\rangle$

$i \neq j$

So only the diagonal terms remain in the sum

low concentration $\left\langle n_i \right\rangle << 1$

$$\left\langle n_i^2 \right\rangle = \left\langle n_i \right\rangle = \left\langle n_1 \right\rangle$$

$$\left\langle (\delta N)^2 \right\rangle = \sum_{i=1}^{m} \left[\left\langle n_i^2 \right\rangle - \left\langle n_i \right\rangle^2 \right] = m \left\langle n_1 \right\rangle \left(1 - \left\langle n_1 \right\rangle\right) \qquad \approx m \left\langle n_1 \right\rangle = \left\langle N \right\rangle$$

can show $\beta p = \rho = \dfrac{\left\langle N \right\rangle}{V} \Rightarrow \boxed{pV = nRT}$

ideal gas law