

Lecture 6

Stat. mech. provides molecular foundations of thermodynamics.

$N \sim 10^{23}$ part. \Rightarrow impossible to follow each particle individually but simplicity emerges since many quantities are described by gaussian distributions with vanishingly small σ 's.
e.g., pressure

Consider a classical system:

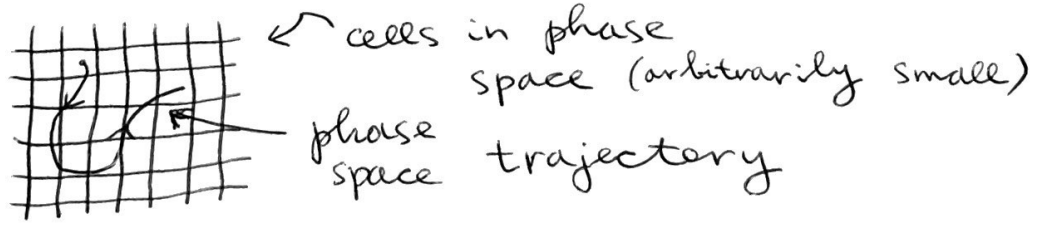
phase space $(\vec{r}_1, \dots, \vec{r}_N; \vec{p}_1, \dots, \vec{p}_N)$
 $6N$ DoF (in 3D)

Systems evolve in time, tracing a trajectory in phase space given by

Hamilton's EoM:
$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} \end{cases} + \text{initial conditions} = \text{full dynamics of the system}$$

H is the Hamiltonian of the system.
total # part.

Suppose we fix E, N, V
tot. en. tot. vol.



Basic assumption: in the $t \rightarrow \infty$ limit, (ergodicity) the system will visit all the microscopic states consistent with the constraints imposed on the system (such as $E, N, V = \text{const}$).

Consider N indep. measurements of some quantity G as the system evolves (each measurement is effectively instantaneous), then

$$\bar{G} = \frac{1}{N} \sum_{a=1}^N G_a$$

value from measurement a

Note that $\bar{G} = \sum_J \underbrace{\frac{N_J}{N}}_{\substack{\text{over} \\ \text{all states} \\ \text{(micro)}}} G_J$ ← # times the system was observed in state J

Introducing $P_J = \frac{N_J}{N}$, we obtain:

$$\bar{G} = \sum_J P_J G_J$$

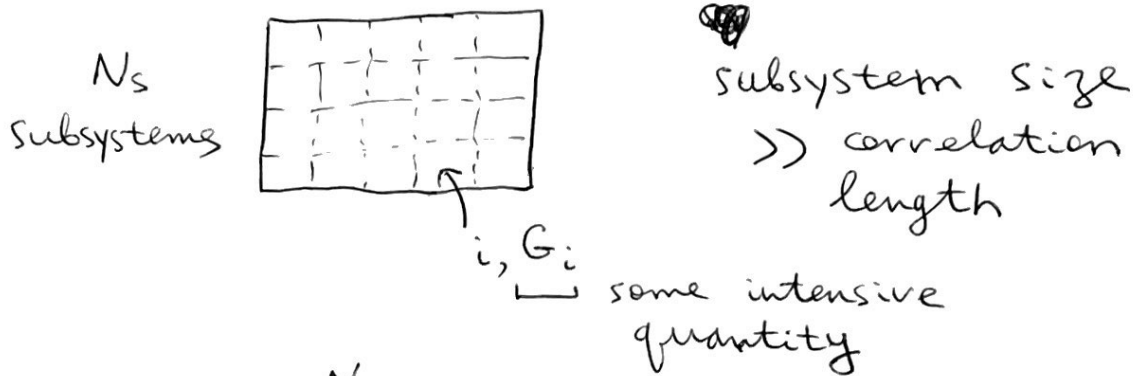
As $t \rightarrow \infty$, \gg relaxation times, all states are visited according to their intrinsic 'weights' P_J^∞ ,

and $\bar{G} \rightarrow \sum_J P_J^\infty G_J \equiv \langle G \rangle$ ensemble average

So, time average = ensemble average
[given enough time]

Ensemble = collection of all possible microstates of the system + probabilities for each microstate.

Ensembles can be 'instantiated' by dividing a macroscopic system into many macroscopic subsystems:



Then $\frac{1}{N_s} \sum_{i=1}^{N_s} G_i = \langle G \rangle$, the ensemble average

Microcanonical ensemble: all microstates with $E, V, N = \text{const}$ (closed isolated system)

Canonical ensemble: $N, V = \text{const}$ but E may fluctuate (closed system in contact with a heat bath)

Grand canonical ensemble: $V = \text{const}$ but E, N may fluctuate (open system)

Microcanonical ensemble

For an isolated system with $E = \text{const}$,
 $V = \text{const}$, $N_i = \text{const}$, $\forall i$, all
microscopic states are equally likely
at thermodynamic equilibrium.

'The most random' situation =
= uniform distribution of microscopic
states.

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

$\delta E =$ energy interval characteristic
of the ability to measure E .

strictly speaking, $\Omega = \Omega_{\delta E}(N, V, E)$,
but it turns out that Ω
is insensitive to δE as long as
 $\delta E < E$, so this dependence is
dropped. $\delta E = 0$ however, Ω is
extremely discontinuous.

Defined this way,

Ω is a continuous function
called the density of states

and $\underbrace{\Omega(N, V, E)dE}_{\text{'macroscopic } dE'}}$ = # states with energy in $[E, E+dE]$ interval

Then
$$\begin{cases} P_0 = \frac{1}{\Omega(N, V, E)} & \text{for all states in the ensemble } (E_0 = E) \\ P_0 = 0 & \text{otherwise } (E_0 \neq E) \end{cases}$$

Define entropy as

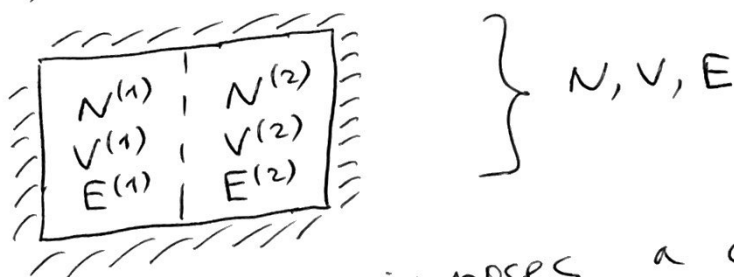
$$S = k_B \log \Omega(N, V, E) \quad (*)$$

$\underbrace{k_B}_{\text{Boltzmann's constant}}$

S is extensive:

$$S_{A+B} = k_B \log(\Omega_A \Omega_B) = S_A + S_B.$$

Moreover, consider



partitioning imposes a constraint:

$$\Omega(N, V, E; \text{constraint}) < \Omega(N, V, E)$$

\Downarrow

$$[S(N, V, E; \text{internal constraint}) < S(N, V, E)$$

2nd law of thermodynamics (!)

Maximization of entropy = maximization of disorder in the system.

Next, consider

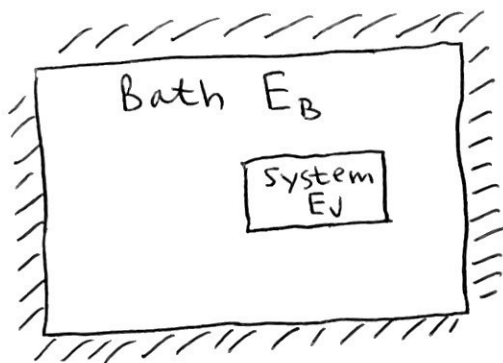
$$\beta = \frac{1}{k_B T} = \frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{N, V} = \left(\frac{\partial \log \Omega}{\partial E} \right)_{N, V}$$

Since $T > 0 \Rightarrow \beta > 0 \Rightarrow \log \Omega$ (or Ω) \uparrow as $E \uparrow$.

Thus, $\left(\frac{\partial \Omega}{\partial E} \right)_{N, V}$ is positive by assumption.

Eq. (*) is a starting point for thermodynamics.

Canonical ensemble



Total $E, N, V = \text{const}$

$$E_B + E_V = E; \quad E_B \gg E_V \text{ by assumption}$$

For the system, $N_S = \text{const}$ & $V_S = \text{const}$ but there is energy exchange.

Since the bath is large, $\Omega_B(E)$ is continuous and $\frac{d\Omega_B(E)}{dE}$ is well-defined.

If the system is in state J , with energy E_J , $\Omega_B(E_B) = \Omega_B(E - E_J)$.

Therefore, $P_J \sim \Omega_B(E - E_J) = e^{\log \Omega_B(E - E_J)}$.

Since $E_J \ll E$,

$$\log \Omega_B(E - E_J) \approx \log \Omega_B(E) - \frac{d \log \Omega_B}{dE} E_J$$

$\log \Omega_B$ is better to expand than Ω_B itself \rightarrow saddle-point like approximation.

Using $\left(\frac{\partial \log \Omega_B}{\partial E}\right)_{N, V} = \beta$, we get
 $P_J \sim e^{-\beta E_J}$ (note that $T_{\text{bath}} = T_{\text{system}}$)

$$\sum_J P_J = 1 \Rightarrow P_J = \frac{e^{-\beta E_J}}{Q}, \text{ where } Q = \sum_J e^{-\beta E_J}$$

$Q = Q(\beta, \underbrace{N_S, V_S}_{E_J \text{ depends on } N_S, V_S \text{ in general}})$ is the canonical partition function

Next, consider

$$\langle E \rangle = \sum_{\nu} P_{\nu} E_{\nu} = \frac{\sum_{\nu} E_{\nu} e^{-\beta E_{\nu}}}{\sum_{\nu'} e^{-\beta E_{\nu'}}} =$$

$$= - \left(\frac{\partial \log Q}{\partial \beta} \right)_{N, V} \quad (*)$$

Note that if we assume that

$$A = -\beta^{-1} \log Q, \quad \langle E \rangle = \left(\frac{\partial(\beta A)}{\partial \beta} \right)_{N, V} \text{ from } (*)$$

On the other hand, thermodynamics gives:

$$\left(\frac{\partial(\beta A)}{\partial \beta} \right)_{N, V} = A + \beta \left(\frac{\partial A}{\partial \beta} \right)_{N, V} = A + \beta \underbrace{\left(\frac{\partial A}{\partial T} \right)_{N, V}}_{-S} \underbrace{\frac{dT}{d\beta}}_{-k_B T^2} =$$

$$= E - TS + \underbrace{T}_{\beta(k_B T^2) = T} S = E.$$

Thus, $E \Leftrightarrow \langle E \rangle$ in this case.

Next, note that

$$Q = \sum_{\substack{\nu \\ \uparrow \\ \text{states}}} e^{-\beta E_{\nu}} = \sum_{\substack{\ell \\ \uparrow \\ \text{energy levels}}} \Omega(E_{\ell}) e^{-\beta E_{\ell}} \rightarrow \int_0^{\infty} dE \underbrace{\Omega(E)}_{\substack{\text{density of} \\ \text{states} \\ \text{(DOS)}}} e^{-\beta E}$$

Thus, Q is the Laplace transform of the DOS.

Energy fluctuations

[canonical ensemble]

Consider $\langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle =$
 $= \langle E^2 \rangle - \langle E \rangle^2 = \sum_{\nu} P_{\nu} E_{\nu}^2 - \left(\sum_{\nu} P_{\nu} E_{\nu} \right)^2 =$

$$= \frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{N, \nu} - \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)_{N, \nu}^2 = \left(\frac{\partial^2 \log Q}{\partial \beta^2} \right)_{N, \nu} \quad \text{⊖}$$

$$P_{\nu} = \frac{e^{-\beta E_{\nu}}}{Q}$$

$$\text{⊖} - \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N, \nu} \quad \left. \vphantom{\frac{\partial \langle E \rangle}{\partial \beta}} \right] \quad \left. \vphantom{\frac{\partial \langle E \rangle}{\partial \beta}} \right]$$

$$\langle E \rangle = - \left(\frac{\partial \log Q}{\partial \beta} \right)_{N, \nu}$$

Recall that $C_V = \left(\frac{\partial E}{\partial T} \right)_{N, \nu}$: 'dissipation'

$$\underbrace{\langle (\delta E)^2 \rangle}_{\text{fluctuations}} = - \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N, \nu} \underbrace{\frac{dT}{d\beta}}_{-k_B T^2} = \underbrace{k_B T^2}_{\text{usually, } (k_B=1)} C_V$$

Next, $\frac{\sqrt{\langle (\delta E^2) \rangle}}{\langle E \rangle} = \frac{\sqrt{k_B T^2 C_V}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}$

$C_V, \langle E \rangle \sim N \leftarrow$ extensive

As $N \uparrow$ ($N \sim 10^{23}$ in macroscopic systems), the fluctuations become unimportant, and

$\langle E \rangle \rightarrow$ microcanonical E obtained
by inserting $\left(\frac{\partial \log \Omega}{\partial E} \right)_{N, V} = \beta(E, N, V)$.

