Stat. mech. provides molecular foundations of thermodynamics.

N ~ $10^{23}$ part. $\Rightarrow$ impossible to follow each particle individually but simplicity emerges since many quantities are described by Gaussian distributions with vanishingly small $\delta'$s.

Consider a classical system:

*phase space* \((r_1, \ldots, r_N; p_1, \ldots, p_N)\)

6N DoF (in 3D)

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

Hamilton's EoM:

\[
\begin{align*}
\frac{dr_i}{dt} &= \frac{\partial H}{\partial p_i}, \\
\frac{dp_i}{dt} &= -\frac{\partial H}{\partial r_i}
\end{align*}
\]

\(H\) is the Hamiltonian of the system.

Suppose we fix \(E, N, V\) \(\Rightarrow\) total # part. \(\Rightarrow\) cells in phase space (arbitrarily small)

\(-1\)
Basic assumption: in the $t \to \infty$ 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 $N$ independent measurements of some quantity $G$ as the system evolves (each measurement is effectively instantaneous), then

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

value from measurement $a$

Note that $\overline{G} = \sum_{j} \frac{N_j}{N} G_j$ over all states in state $j$.

Introducing $P_j = \frac{N_j}{N}$, we obtain:

$$
\overline{G} = \sum_{j} P_j G_j
$$

$\Rightarrow$ relaxation times

As $t \to \infty$, all states are revisited according to their intrinsic 'weights' $P_j$.

and $\overline{G} \to \sum_{j} P_j \infty G_j \equiv \langle G \rangle$

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:

\[ N_s \] subsystems

\[ \text{subsystem size} \gg \text{correlation length} \]

\[ i, G_i \] some intensive quantity

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 $E = \text{const}$, $V = \text{const}$, $N_i = \text{const}$, and all chemical species $i$, microscopic states are equally likely at thermodynamic equilibrium.

The most random situation = uniform distribution of microscopic states.

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

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

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

Defined this way, $\Omega$ is a continuous function called the density of states.
and \( \mathcal{N}(N, V, E) dE = \# \text{ states with energy} \]

'macroscopic dE'

in \([E, E+dE]\)

interval

Then \[
\begin{cases}
P_v = \frac{1}{\mathcal{N}(N, V, E)} & \text{for all states in the ensemble } (E_v = E) \\
P_v = 0 & \text{otherwise } (E_v \neq E)
\end{cases}
\]

Define entropy as

\[
S = k_B \log \mathcal{N}(N, V, E) \quad (*)
\]

Boltzmann's constant

\(S\) is extensive:

\[
S_{A+B} = k_B \log (\mathcal{N}_A \mathcal{N}_B) = S_A + S_B.
\]

Moreover, consider

\[
\begin{array}{c|c}
N^{(1)} & N^{(2)} \\
V^{(1)} & V^{(2)} \\
E^{(1)} & E^{(2)}
\end{array}
\]

partitioning imposes a constraint:

\[
\mathcal{N}(N, V, E ; \text{constraint}) < \mathcal{N}(N, E, V) \quad \downarrow
\]

\[
\begin{bmatrix}
S(N, V, E ; \text{internal constraint}) < S(N, V, E)
\end{bmatrix}
\]

2nd law of thermodynamics (?)

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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 \( S \)) \( \uparrow \)
as \( E \) \( \uparrow \).

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

Eq. (\( \ast \)) is a starting point for thermodynamics.

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**Canonical ensemble**

\[ \text{Bath } E_B \quad \begin{cases} \text{Total} \\ E, N, V = \text{const} \end{cases} \]

\[ E_B + E_s = E \quad \text{by assumption} \]

For the system, \( N_s = \text{const} \) and \( V_s = \text{const} \) but there is energy exchange.
Since the bath is large, $\mathcal{R}_b(E)$ is continuous and $\frac{d\mathcal{R}_b(E)}{dE}$ is well-defined.

If the system is in state $j_0$ with energy $E_{j_0}$, $\mathcal{R}_b(E_{j_0}) = \mathcal{R}_b(E - E_{j_0})$.

Therefore, $P_{j_0} = \mathcal{R}_b(E - E_{j_0}) = e^\log \mathcal{R}_b(E - E_{j_0})$.

Since $E_{j_0} \ll E$,

$$\log \mathcal{R}_b(E - E_{j_0}) = \log \mathcal{R}_b(E) - \frac{d\log \mathcal{R}_b(E)}{dE} E_{j_0}$$

$\log \mathcal{R}_b$ is better to expand than $\mathcal{R}_b$ itself → saddle-point like approximation.

Using $\left(\frac{\partial \log \mathcal{R}_b}{\partial E}\right)_{N, V} = \beta$, we get

$$P_{j_0} \sim e^{-\beta E_{j_0}}$$

(note that $T_{\text{bath}} = T_{\text{system}}$)

$$\sum_j P_{j_0} = 1 \Rightarrow P_{j_0} = \frac{e^{-\beta E_{j_0}}}{Q}, \quad \text{where}$$

$$Q = \sum_j e^{-\beta E_{j_0}}.$$

$Q = Q(\beta, N_s, V_s)$ is the canonical partition function

$E_{j_0}$ depends on $N_s, V_s$ in general.
Next, consider

\[ \langle E \rangle = \sum \mathcal{P}_j \ E_j = \frac{\sum \mathcal{E}_j \ e^{-\beta E_j}}{\sum \ e^{-\beta E_j}} = \]

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

Note that if we assume that

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

On the other hand, thermodynamics gives:

\[ \left( \frac{\partial (\beta A)}{\partial \beta} \right)_{N, V} = A + \beta \left( \frac{\partial A}{\partial T} \right)_{N, V} \frac{dT}{\beta} = \]

\[ = E - TS + TS = E \]

\[ \beta (k_B T^2) = T \]

Thus, \[ E \leftrightarrow \langle E \rangle \] in this case.

Next, note that

\[ Q = \sum \mathcal{E}_j \ e^{-\beta E_j} = \sum \mathcal{N}(E_x) \ e^{-\beta E_x} \rightarrow \int dE \mathcal{N}(E) \ e^{-\beta E} \]

Thus, \[ Q \] is the Laplace transform of the DoS.
Energy fluctuations
[canonical ensemble]

Consider \(<(\delta E)^2> = <(E - <E>)^2> = \)
\[ = <E^2> - <E>^2 = \sum_p P_v E_v^2 - \left( \sum_p P_v E_v \right)^2 = \]
\[ = \frac{1}{Q} \left( \frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} - \frac{1}{Q^2} \left( \frac{\partial Q}{\partial \beta} \right)^2_{N,V} = \left( \frac{\partial^2 \log Q}{\partial \beta^2} \right)_{N,V} \]
\[ P_v = \frac{e^{-\beta E_v}}{Q} \]
\[ \equiv - \left( \frac{\partial <E>}{\partial \beta} \right)_{N,V}. \]
\[ <E> = - \left( \frac{\partial \log Q}{\partial \beta} \right)_{N,V} \]

Recall that \( C_V = \left( \frac{\partial E}{\partial T} \right)_{N,V} \): 'dissipation',
\[ <(\delta E)^2> = - \left( \frac{\partial <E>}{\partial T} \right)_{N,V} \frac{dT}{dB} = k_B T^2 C_V \]

fluctuations

Next, \( \frac{\sqrt{<(\delta E)^2>}}{<E>} = \frac{\sqrt{k_B T^2 C_V}}{<E>} \sim \frac{1}{\sqrt{N}} \)
\[ C_V, <E> \sim N \sim \text{extensive} \]

As \( N^2 \) (\( N \sim 10^{21} \) in macroscopic systems), the fluctuations become unimportant, and
$\langle E \rangle \rightarrow \text{microcanonical } E \text{ obtained by inserting } \left( \frac{\partial \log Z}{\partial E} \right)_{N,V}^{} = \beta(E, N, V)$. 

\[ \]

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