

Kardar,
ch. 4

Classical Statistical Mechanics

Statistical Mechanics — A probabilistic approach to understanding equilibrium macroscopic properties of large numbers of degrees of freedom.

Macrostate M — described by small number of thermodynamic coordinates, phenomenological laws.

Microstate μ — described by enormous amount of information, governed by Hamiltonian evolution.

$\mu \rightarrow M$ many-to-one map

Consider an ensemble of microstates corresponding to a given macrostate

We want the probabilities $P_M(\mu)$ for the equilibrium ensemble.

Liouville's theorem \rightarrow In equilibrium $\{P_{eq}, H\} = 0$.

Solved by $P_{eq}(\vec{p}, \vec{q}) = P_{eq}(H(\vec{p}, \vec{q}))$. (Other solutions might exist.)

Other conserved quantities L_n satisfy $\{L_n, H\} = 0$

\rightarrow can have $P_{eq} = P_{eq}(H(\vec{p}, \vec{q}), L_1(\vec{p}, \vec{q}), L_2(\vec{p}, \vec{q}), \dots)$

\rightarrow All accessible microstates are equally likely in an equilibrium ensemble.

Microcanonical Ensemble

Consider a mechanically and adiabatically isolated system (i.e. no work is done on or by the system, and no heat is transferred.)

Internal energy E is fixed, generalized coordinates fixed.

$$\text{Microstate } M \equiv (E, \vec{x})$$

↑ generalized coordinates

Corresponding set of mixed microstates form the microcanonical ensemble.

Microstates are confined to the surface

$$\mathcal{H}(\mu) = E \text{ in phase space.}$$

(For now, assume no other conserved quantities.)

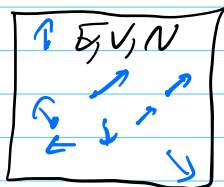
Central postulate of Stat Mech:

$$P_{(E, \vec{x})}(\mu) = \frac{1}{\Omega(E, \vec{x})} \cdot \begin{cases} 1 & \text{if } \mathcal{H}(\mu) = E \\ 0 & \text{otherwise.} \end{cases}$$

↑
Normalization factor

$\Omega(E, \vec{x})$: area of surface of constant E in phase space.

Example: Ideal gas



E, V, N fixed

$$\sum_{i=1}^N \vec{p}_i^2 = 2mE$$

constant $-E$ surface.

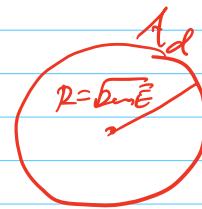
$(3N-1)$ -dimensional sphere of radius $\sqrt{2mE}$.

Area of $(d-1)$ -dimensional sphere:

Kardar's notation for $(d-1)$ -dimensional sphere embedded in d dimensions.

$$\rightarrow A_d = S_d R^{d-1}$$

← radius
generalized solid angle



Aside: S_d from Gaussian integrals

$$\text{Consider } I_d = \left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^d = \boxed{\pi^{d/2}}$$

$$= \int dx_1 \dots dx_d \exp\left(-\sum_{i=1}^d x_i^2\right)$$

$$= \int_0^{\infty} dR R^{d-1} S_d e^{-R^2} \quad \text{"spherical" coords.}$$

$$y=R^2 = \frac{S_d}{2} \int_0^{\infty} dy y^{d/2-1} e^{-y^2}$$

$$= \frac{S_d}{2} \Gamma(d/2)$$

$$\left(= \frac{S_d}{2} \left(\frac{d}{2}-1\right)! \right)$$

$$\rightarrow S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} = \frac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}$$

$$\Gamma(n) = (n-1)!$$

$$\Gamma(1/2) = \sqrt{\pi}$$

$$\Gamma(x+1) = x \Gamma(x)$$

2-sphere $x^2 + y^2 + z^2 = R^2$ — embedded in 3 dimensions
 $\rightarrow d=3$

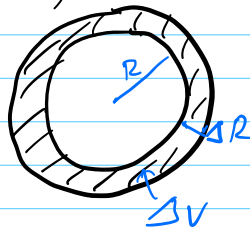
$$A_3 = \frac{2\pi^{3/2}}{\Gamma(\frac{3}{2})} R^2 = \frac{2\pi^{3/2}}{\frac{1}{2}\pi^{1/2}} R^2 = 4\pi R^2$$

↑
 S_3

So, the area of allowed phase space is

$$\Omega(E, V, N) = V^N \frac{(2mE)^{\frac{3N-1}{2}} (2\pi^{3/2})}{\Gamma(\frac{3N}{2})}$$

Sometimes we may want to consider the phase space volume in a shell of Energy between $(E - \Delta E, E + \Delta E)$



$$\Delta V_d = A_d(\Delta R)$$

$$2\text{-sphere: } \Delta V_3 = (4\pi R^2) \Delta R$$

$$R = \sqrt{2mE} \rightarrow \Delta R = \sqrt{\frac{m}{2E}} (2\Delta E)$$

$$\Omega(E, V, N) = V^N \frac{2\pi^{3N/2}}{\Gamma(\frac{3N}{2})} (2mE)^{\frac{(3N-1)}{2}} \Delta R$$

Entropy: $P_{(E, \vec{x})}(m) = \frac{1}{\Omega(E, \vec{x})} \cdot \begin{cases} 1 & \text{if } \mathcal{H}(m) = E \\ 0 & \text{otherwise} \end{cases}$

$$S \equiv -k_B \sum_m P(m) \ln P(m)$$

$$= k_B \left(\sum_m \frac{1}{\Omega(E, \vec{x})} \right) \ln \Omega(E, \vec{x})$$

$$S = k_B \ln \Omega(E, \vec{x})$$

Boltzmann's constant

Ideal gas:

$$S = k_B \ln \left[V^N (2\pi m E)^{\frac{3N}{2}} (2mE)^{-1/2} \right] - k_B \ln \left(\frac{3N}{2} - 1 \right)!$$

$$S \xrightarrow{N \gg 1} N k_B \ln \left[V (2\pi m E)^{\frac{3}{2}} \right] - k_B \left(\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right)$$

$$S = N k_B \ln \left[V \left(\frac{4\pi m E e}{2N} \right)^{\frac{3}{2}} \right]$$

Use thermodynamic relations to determine thermodynamic coordinates:

$$T dS = dE + PdV - \mu dN$$

$$\rightarrow \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{3}{2} \frac{N k_B}{E}$$

$$\rightarrow E = \frac{3}{2} N k_B T$$

Heat Capacity: $C_V = T \left. \frac{\partial S}{\partial T} \right|_{V, N} = \left. \frac{\partial E}{\partial T} \right|_{V, N}$

$$C_V = \frac{3}{2} N k_B$$

Equation of State: $\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E, N} = \frac{N k_B}{V}$

$$PV = N k_B T$$

Unconditional probability of finding that a given particle has momentum between $(\vec{p}_1, \vec{p}_1 + d\vec{p}_1)$: $P(\vec{p}_1) d^3 p_1$

$$P(\vec{p}_1) = \int d\vec{q}_1 \left(\prod_{i=2}^N \int d\vec{q}_i \int d\vec{p}_i P(\{\vec{q}_i, \vec{p}_i\}) \right)$$

$$= V \frac{\Omega(E - \vec{p}_1^2 / 2m, V, N-1)}{\Omega(E, V, N)}$$

Energy of remaining $N-1$ particles

$$= V^N \frac{\pi^{3(N-1)/2} (2mE - \vec{p}_1^2)^{(3N-4)/2}}{\Gamma\left(\frac{3(N-1)}{2}\right)} \cdot \frac{\Gamma\left(\frac{3N}{2}\right)}{V^N \pi^{3N/2} (2mE)^{3N/2}}$$

$$= \left(1 - \frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2}-2} \frac{1}{(2\pi mE)^{3/2}} \frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3(N-1)}{2}\right)}$$

$$\stackrel{N \gg 1}{\sim} \left(1 - \frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2}} \frac{1}{(2\pi mE)^{3/2}} \frac{\left(\frac{3(N-1)}{2}\right)^{2(N-1)/2}}{\left(\frac{3(N-2)}{2}\right)^{2(N-2)/2}}$$

$$P(\vec{p}_1) \propto \left(1 - \frac{\vec{p}_1^2}{2mE}\right) \frac{1}{(2\pi m E)^{3/2}} \left(\frac{3N}{2}\right)^{3/2}$$

For $\vec{p}_1^2 \ll 2mE$,

$$P(\vec{p}_1) \approx \left(\frac{3N}{2\pi m E}\right)^{3/2} \exp\left(-\frac{3N}{2} \frac{\vec{p}_1^2}{2mE}\right)$$

Using $E = \frac{3}{2} N k_B T$,

$$P(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{\vec{p}_1^2}{2m k_B T}\right)$$

Maxwell-Boltzmann Distribution

Extensivity and identical particles

We found the entropy of the ideal gas to be

$$S(E, V, N) = N k_B \ln \left[V \left(\frac{4\pi m E e}{3N} \right)^{3/2} \right]$$

Because of the factor of V in the log, this expression is not extensive:

$$A_S(E, V, N) \rightarrow (\lambda E, \lambda V, \lambda N),$$

$$S \rightarrow \lambda N k_B \ln \left[\lambda V \left(\frac{4\pi m (\lambda E) e}{3(\lambda N)} \right)^{3/2} \right]$$

$$= \lambda (S + N k_B \ln \lambda)$$

We treated the N particles in the gas as distinguishable.

If the particles are identical then we have overcounted the allowed phase space by the $N!$ permutations of the particles corresponding to the same microstate.

Dividing our previous expression for $\Omega(E, V, N)$ by $N!$, we now have:

$$\Omega(E, V, N) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (2mE)^{\frac{3N-1}{2}}$$

The entropy is now

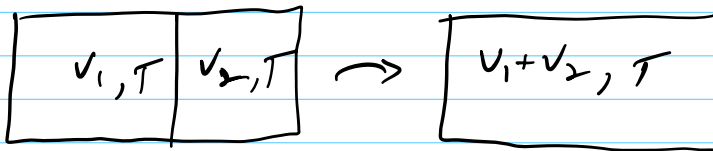
$$S = k_B \ln \Omega(E, V, N)$$
$$\stackrel{(N \rightarrow \infty)}{=} N k_B \ln \left[V \left(\frac{4\pi m E e}{3N} \right)^{3/2} \right]$$
$$- \frac{k_B}{N} (N \ln N - N)$$

$$S = N k_B \ln \left[\frac{V e}{N} \left(\frac{4\pi m E e}{3N} \right)^{3/2} \right]$$

With the extra factor of $\frac{1}{N}$ in the log, S is now extensive.

Mixing Entropy and the Gibbs Paradox

When two distinct gases are mixed, there is an associated increase in entropy, the mixing entropy.



The entropy of the two gases separated by a partition is

$$S_{\text{initial}} = S_1 + S_2 = N_1 k_B \left[\ln V_1 + \sigma_1 \right] + N_2 k_B \left[\ln V_2 + \sigma_2 \right]$$

$$\text{where } \sigma_\alpha = \ln \left(\frac{4\pi m_\alpha E_\alpha e}{3 N_\alpha} \right), \alpha = 1, 2$$

$$\text{Since } E_\alpha = \frac{3}{2} N_\alpha k_B T,$$

$$\sigma_\alpha(T) = \frac{3}{2} \ln(2\pi e m_\alpha k_B T)$$

Removing the partition, the gases mix but the temperature stays the same:

$$\frac{3}{2} k_B T_{\text{final}} = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T$$

After mixing, the entropy is:

$$S_{\text{final}} = N_1 k_B \ln(V_1 + V_2) + N_2 k_B \ln(V_1 + V_2) + k_B (N_1 \sigma_1 + N_2 \sigma_2)$$

The increase in entropy due to mixing is:

$$\Delta S_{\text{mix}} = S_{\text{final}} - S_{\text{initial}}$$
$$= N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2}$$

$$= -N k_B \left[\frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right]$$

If we use the same expression for the entropy when the gases are identical, with the same density $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$,

then removing the partition does nothing to the gases macroscopically, but we would find $\Delta S_{\text{mix}} \neq 0$.

This is the Gibbs paradox.

The resolution is to use the entropy appropriate for identical particles:

$$\Delta S_{\text{mix}} = (N_1 + N_2) k_B \ln \frac{V_1 + V_2}{N_1 + N_2}$$
$$- \left(N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V_2}{N_2} \right)$$
$$= 0 \quad \text{if} \quad \frac{N_1}{V_1} = \frac{N_2}{V_2}.$$