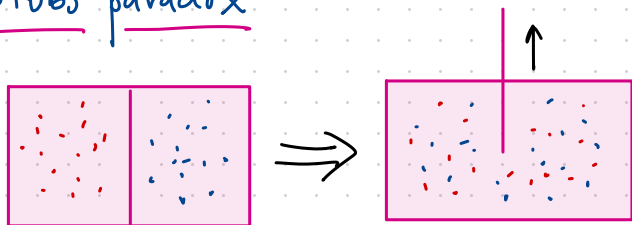


Gibbs paradox



Before the $N!$ correction

$$S(E, V, N) = N k_B \ln(V \square),$$

$$\square = \left(\frac{4\pi m E}{3N} \right)^{3/2}$$

$$S_{\text{initial}} = N_1 k_B \ln(V_1 \square_1) + N_2 k_B \ln(V_2 \square_2)$$

$$S_{\text{final}} = N_1 k_B \ln(V \square_1) + N_2 k_B \ln(V \square_2), \quad V = V_1 + V_2$$

$$\therefore \Delta S_{\text{mix}} = S_{\text{final}} - S_{\text{initial}}$$

$$= N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2}$$

$$\text{If } V = 2V_1 = 2V_2, \Delta S_{\text{mix}} = N k_B \ln 2$$

So far so good, but what if the two gases are actually identical, the entropy should not change?

Let us see what happens after the $N!$ correction.

$$S(E, V, N) = N k_B \ln \left(\frac{V}{N} e \square \right)$$

Case I: Non-identical gas

$$\left. \begin{aligned} S_{\text{initial}} &= N_1 k_B \ln \left(\frac{V_1}{N_1} e \square_1 \right) + N_2 k_B \ln \left(\frac{V_2}{N_2} e \square_2 \right) \\ S_{\text{final}} &= N_1 k_B \ln \left(\frac{V}{N_1} e \square_1 \right) + N_2 k_B \ln \left(\frac{V}{N_2} e \square_2 \right) \end{aligned} \right\} \begin{array}{l} \text{Same} \\ \Delta S_{\text{mix}} \end{array}$$

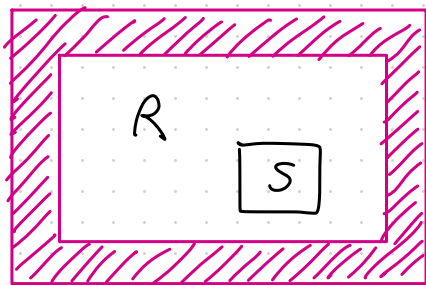
Case II: Identical gases with the same density

$$n = \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$$

$$\begin{aligned}\Delta S_{\text{mix}} &= (N_1 + N_2) k_B \ln \frac{V_1 + V_2}{N_1 + N_2} - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} \\ &= -(N_1 + N_2) k_B \ln n + (N_1 + N_2) k_B \ln n = 0\end{aligned}$$

Canonical ensemble

In a microcanonical ensemble, the system is isolated from the rest of the universe. Consequently, the energy E of the system can be precisely specified. The temperature T is then a derived quantity.



"Heat Bath"

But usually it is easier to control for the temperature T by putting our system of interest in a thermal contact with a large "reservoir" of temperature T (after which our system will quickly equilibrate to have the same temperature T).

	System	Reservoir
Microstate	μ_S	μ_R
Hamiltonian	H_S	H_R
Energy	$H_S(\mu_S) = E_S$	$H_R(\mu_R) = E_R$

(Large reservoir assumption) $E_S \ll E_R$

Our first main goal is to derive the probability that the system S is in a microstate μ_S with energy $E_S = H(\mu_S)$.

We start by assuming that the combined system $S+R$ is isolated from the rest of the universe. Therefore, the joint state (joint probability distribution) can be described by the microcanonical ensemble

$$\left(\begin{array}{c} \text{Joint} \\ \text{PDF} \end{array} \right) p_{SR}(\mu_S, \mu_R) = \frac{1}{\Omega_{SR}(E_{\text{tot}})} \cdot \begin{cases} 1, & H_S(\mu_S) + H_R(\mu_R) = E_{\text{tot}} \\ 0, & \text{otherwise} \end{cases}$$

We want the unconditional probability for the state of the system

$$p_S(\mu_S) = \int d\Gamma_R p_{SR}(\mu_S, \mu_R)$$

Integrating over
all microstates
of R in the
ensemble

$$= \frac{\Omega_R(E_{\text{tot}} - E_S)}{\Omega_{SR}(E_{\text{tot}})}$$

The numerator
is proportional
to

$$\propto e^{S_R(E_{\text{tot}} - E_S)/k_B}$$

Since $E_{\text{tot}} \gg E_S$ we can Taylor expand the entropy around E_{tot} .

Recall Taylor expansion in 1D:

$$f(x) = f(a) + (x-a) \frac{df}{dx} \Big|_a + \frac{(x-a)^2}{2!} \frac{d^2f}{dx^2} \Big|_a + \dots$$

$$S_R(E_{\text{tot}} - E_S) \approx S_R(E_{\text{tot}}) - E_S \frac{\partial S_R}{\partial E_R} = S_R(E_{\text{tot}}) - \frac{E_S}{T}$$

$$\Rightarrow p_S(\mu_S) \propto e^{-E_S/k_B T}$$

since $S_R(E_{\text{tot}})$ is independent
of the microstate μ_S

Dropping the S subscript, we conclude that the probability that the system in contact with a heat bath at temperature T to be in a microstate μ with energy $H(\mu)$ is given by

$$p(\mu) = \frac{e^{-H(\mu)/k_B T}}{Z}$$

$$Z = \sum_{\mu} e^{-H(\mu)/k_B T}$$

Partition Function

(Continuous coordinates example)

$$Z = \int \prod_{j=1}^N d^3 q_j d^3 p_j e^{-[\sum_j p_j^2/2m + V(\vec{q})]/k_B T}$$

It will be handy to define $\beta = 1/k_B T$

	Macrostate	$p(\mu)$	Free energy
Micro-canonical	(E, \vec{x})	$\frac{1}{\Omega} \cdot \begin{cases} 1, & \text{if } H(\mu) = E \\ 0, & \text{otherwise} \end{cases}$	$S = k_B \ln \Omega$
Canonical	(T, \vec{x})	$\frac{e^{-\beta H(\mu)}}{Z}$	$F = -k_B T \ln Z$

All of thermodynamics "slide down" from these normalization factors we gave the fancy name "partition Functions".

This is the reason the complexity of calculating the partition function is a big deal and is a subject of study in classical and quantum computer science.

Mean energy

$$\langle E \rangle = \sum_j E_j p_j = \sum_j E_j \frac{e^{-\beta E_j}}{Z} = \boxed{-\frac{\partial \ln Z}{\partial \beta}}$$

The variance is related to the specific heat

$$N C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{d\beta}{dT} = -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial \beta} &= \frac{\partial}{\partial \beta} \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \\ &= \frac{-\sum_j E_j^2 e^{-\beta E_j}}{Z} + \frac{(\sum_j E_j e^{-\beta E_j})^2}{Z^2} \\ &= -\langle E^2 \rangle + \langle E \rangle^2 = -\sigma_E^2 \end{aligned}$$

$$\Rightarrow \boxed{N C_V = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\sigma_E^2}{k_B T^2}}$$

$$\sigma_E = \sqrt{N k_B T C_V} \Rightarrow \left(\begin{array}{c} \text{Relative} \\ \text{error} \end{array} \right) \frac{\sigma_E}{\langle E \rangle} \propto \frac{\sigma_E}{N} = \sqrt{\frac{k_B T C_V}{N}}$$

Energy fluctuation vanishes in the limit $N \rightarrow \infty$.

\Rightarrow Canonical and microcanonical ensembles give the same result unless C_V diverges \Leftarrow Phase transition! (2nd half of this course)

Entropy

$$S = -k_B \sum_j p_j \ln p_j = -k_B \sum_j p_j \ln \left(\frac{e^{-\beta E_j}}{Z} \right)$$

$$= -k_B \left[-\beta \sum_j p_j E_j - \sum_j p_j \ln Z \right] = \frac{\langle E \rangle}{T} + k_B \ln Z$$

(Helmholtz
free energy)

$$F := -k_B T \ln Z = \langle E \rangle - TS$$

What is the physical meaning of F ?

$$p(E) = \sum_{\mu} p(\mu) \delta_{H(\mu), E} = \frac{e^{-\beta E}}{Z} \sum_{\mu} \delta_{H(\mu), E} \quad \Omega(E)$$

$$= \frac{\Omega(E) e^{-\beta E}}{Z} = \frac{1}{Z} e^{S(E)/k_B - \beta E} = \frac{1}{Z} e^{-\beta F(E)}$$

meaning that $p(E)$ peaks when the free energy is minimum.

Easy to obtain S once we have F :

$$S = - \left. \frac{\partial F}{\partial T} \right|_{N, V} \quad \blacksquare \quad \left. \frac{\partial F}{\partial T} \right|_{N, V} = -k_B \frac{\partial (T \ln Z)}{\partial T}$$

$$= -k_B \ln Z - k_B T \frac{\partial \ln Z}{\partial T}$$

$$\quad \quad \quad \underbrace{-\langle E \rangle}_{\text{}} \quad \underbrace{-1/k_B T^2}_{\text{}}$$

$$\text{But } -k_B T \frac{\partial \ln Z}{\partial T} = -k_B T \frac{\partial \ln Z}{\partial \beta} \frac{d\beta}{dT} = -\frac{\langle E \rangle}{T}$$

$$\therefore \left. \frac{\partial F}{\partial T} \right|_{N, V} = - \left(\frac{\langle E \rangle}{T} + k_B \ln Z \right) = -S \quad \checkmark$$

□