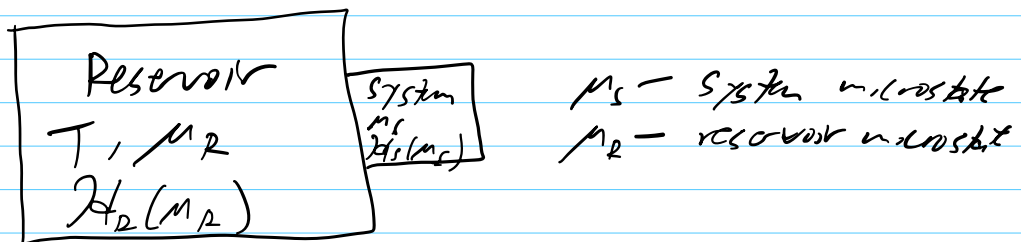


The Canonical Ensemble

Rather than specify the energy E and determine the temperature T , we can consider an ensemble with temperature T and deduce the internal energy E .

In the canonical ensemble macrostates are specified by $M \equiv (T, \bar{x})$, and we allow the input of heat into the system to maintain temp. T , but no work.



Reservoir with $E_R \gg E_S$, so that T is not changed significantly due to interactions with system.

Probability of microstates

$$P(\mu_S \otimes \mu_R) = \frac{1}{\Omega_{S \otimes R}(E_{\text{tot}})} \begin{cases} 1 & \text{for } \mathcal{H}_S(\mu_S) + \mathcal{H}_R(\mu_R) = E_{\text{tot}} \\ 0 & \text{otherwise} \end{cases}$$

Unconditional probability for microstates μ_S ?

$$P(\mu_S) = \sum_{\substack{\mu_R, \\ E_R = E_{\text{tot}} - \mathcal{H}_S(\mu_S)}} P(\mu_S \otimes \mu_R)$$

$$P(\mu_s) = \frac{\Omega_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_s))}{\Omega_{\text{SQR}}(E_{\text{Tot}})}$$

$$\propto \exp\left[\frac{1}{k_B} S_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_s))\right]$$

↑ entropy of reservoir at appropriate energy.

Expand:

$$S_R(E_{\text{Tot}} - \mathcal{H}_S(\mu_s)) \approx S_R(E_{\text{Tot}}) - \frac{\partial S_R}{\partial E_R} \mathcal{H}_S(\mu_s)$$

$$= S_R(E_{\text{Tot}}) - \frac{1}{T} \mathcal{H}_S(\mu_s)$$

↑ fixed

↑ depends on microstate

$$P_{(T, \bar{x})}(\mu_s) = \frac{e^{-\beta \mathcal{H}(\mu_s)}}{Z(T, \bar{x})}$$

Normalization factor

$$Z(T, \bar{x}) = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)}$$

partition function

$$\beta \equiv 1/k_B T$$

Internal energy E has probability distribution

$$P(E) = \sum_{\mu} P(\mu) \delta(\mathcal{H}(\mu) - E) = \frac{e^{-\beta E}}{Z} \sum_{\mu} \delta(\mathcal{H}(\mu) - E)$$

↑
Replacing the 'S' for system

$$= \frac{e^{-\beta E}}{Z} \Omega(E)$$

$$p(\epsilon) = \frac{1}{Z} \exp \left[\frac{S(\epsilon)}{k_B} - \frac{\epsilon}{k_B T} \right]$$

$$= \frac{1}{Z} \exp \left[- \frac{F(\epsilon)}{k_B T} \right]$$

where $F(\epsilon) = \epsilon - TS(\epsilon)$

$p(\epsilon)$ is peaked around the most probable energy ϵ^* , which minimizes $F(\epsilon)$.

$$\left. \frac{\partial F}{\partial \epsilon} \right|_{\epsilon = \epsilon^*} = 0.$$

$$Z = \sum_m e^{-\beta \mathcal{H}(m)} = \sum_{\epsilon} e^{-\beta F(\epsilon)} \approx e^{-\beta F(\epsilon^*)}$$

Average energy:

$$\langle \mathcal{H} \rangle = \frac{\sum_m \mathcal{H}(m) e^{-\beta \mathcal{H}(m)}}{Z} = - \frac{1}{Z} \frac{\partial}{\partial \beta} \sum_m e^{-\beta \mathcal{H}(m)}$$

$$\langle \mathcal{H} \rangle = - \frac{\partial}{\partial \beta} \ln Z$$

c.f. Thermo: $E = F + TS = F - T \left. \frac{\partial F}{\partial T} \right|_{\vec{x}}$ $\leftarrow dF = -SdT + \sum_i dx_i$
 $T \mu dN$

$$= -T^2 \left. \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right|_{\vec{x}} = \left. \frac{\partial(\beta F)}{\partial \beta} \right|_{\vec{x}}$$

\leadsto Identity $F(T, \vec{x}) = -k_B T \ln Z(T, \vec{x})$

Helmholtz free energy.

How close are the peak of the distribution $p(\mathcal{H})$ and the mean?

We can calculate the variance of the distribution as follows:

$$-\frac{\partial Z}{\partial \beta} = \sum_{\mathcal{H}} \mathcal{H} e^{-\beta \mathcal{H}}, \quad \frac{\partial^2 Z}{\partial \beta^2} = \sum_{\mathcal{H}} \mathcal{H}^2 e^{-\beta \mathcal{H}}$$

$$\langle \mathcal{H} \rangle_c = \frac{1}{Z} \sum_{\mathcal{H}} \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\langle \mathcal{H}^2 \rangle_c = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$$

$$= \frac{1}{Z} \sum_{\mathcal{H}} \mathcal{H}^2 e^{-\beta \mathcal{H}} - \frac{1}{Z^2} \left(\sum_{\mathcal{H}} \mathcal{H} e^{-\beta \mathcal{H}} \right)^2$$

$$= \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta}$$

n^{th} cumulant: $\langle \mathcal{H}^n \rangle_c = (-1)^n \frac{\partial^n \ln Z}{\partial \beta^n}$

→ Z is like characteristic function for \mathcal{H} .

Variance:

$$\langle \mathcal{H}^2 \rangle_c = -\frac{\partial \langle \mathcal{H} \rangle}{\partial (1/k_B T)} \bigg|_{\mathcal{H}} = k_B T^2 \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \bigg|_{\mathcal{H}}$$

$$= k_B T^2 C_{\mathcal{H}}$$

↪ Heat capacity

Since $C_X \propto N$ and $\langle X \rangle \propto N$,

$$\frac{\sqrt{\langle X^2 \rangle_c}}{\langle X \rangle} \propto \frac{\sqrt{N}}{N} \rightarrow 0 \text{ as } N \rightarrow \infty$$

in thermodynamic limit.

Note that $\langle X^{n+1} \rangle_c = (-1)^n \frac{\partial^n \langle X \rangle}{\partial \beta^n} \propto N$

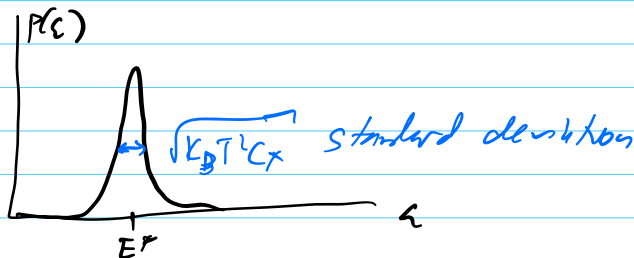
$$\text{so } \frac{(\langle X^{n+1} \rangle_c)^{1/n+1}}{\langle X \rangle} \rightarrow 0 \text{ as } N \rightarrow \infty$$

for $n > 1$

Hence, $p(\xi)$ is approximately Gaussian,

$$p(\xi) = \frac{1}{Z} e^{-\beta F(\xi)}$$

$$\approx \exp\left(-\frac{(\xi - \langle X \rangle)^2}{2k_B T^2 C_X}\right) \cdot \frac{1}{\sqrt{2\pi k_B T^2 C_X}}$$



$\star N \rightarrow \infty$: $p(\xi)$ highly peaked \rightarrow Canonical, microcanonical ensembles become equivalent.

$$\begin{aligned}
 \text{Entropy: } S &= -k_B \langle \ln p(m) \rangle \\
 &= -k_B \langle (-\beta H - \ln Z) \rangle \\
 &= \frac{E - F}{T}
 \end{aligned}$$

Example: Two-Level System

Macrostate specified by $M = (T, N)$.

$$\text{Hamiltonian } H = \epsilon \sum_{i=1}^N n_i$$

$$p(\{n_i\}) = \frac{1}{Z} \exp\left[-\beta \epsilon \sum_{i=1}^N n_i\right]$$

$$Z(T, N) = \sum_{\{n_i\}} \exp\left[-\beta \epsilon \sum_{i=1}^N n_i\right]$$

$$= \left(\sum_{n_1=0}^1 e^{-\beta \epsilon n_1} \right) \left(\sum_{n_2=0}^1 e^{-\beta \epsilon n_2} \right) \dots \left(\sum_{n_N=0}^1 e^{-\beta \epsilon n_N} \right)$$

$$Z = (1 + e^{-\beta \epsilon})^N$$

Free energy

$$F(T, N) = -k_B T \ln Z = -N k_B T \ln [1 + e^{-\beta \epsilon}]$$

$$F = -N k_B T \ln \left[1 + e^{-\epsilon/k_B T} \right]$$

Entropy

$$S = - \frac{\partial E}{\partial T} \Big|_N$$

$$S = Nk_B \ln [1 + e^{-\epsilon/k_B T}] + Nk_B T \left(\frac{\epsilon}{k_B T^2} \right) \frac{e^{-\epsilon/k_B T}}{1 + e^{-\epsilon/k_B T}}$$

Internal Energy

$$E = F + TS = \frac{N \epsilon e^{-\epsilon/k_B T}}{1 + e^{-\epsilon/k_B T}}$$

$$\left(= - \frac{\partial \ln Z}{\partial \beta} \right)$$

Joint probability $p = \prod_{i=1}^N p_i$,

$$P_i(n_i) = \frac{e^{-\beta \epsilon n_i}}{1 + e^{-\beta \epsilon}}, \quad n_i = 0 \text{ or } 1$$

- Same as in microcanonical ensemble.

Example: Ideal Gas

Macrostates $M = (T, V, N)$

Microstates $\mu = \{\vec{p}_i, \vec{q}_i\}$

$$P(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m}\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \text{ in box} \\ 0 & \text{otherwise.} \end{cases}$$

Partition Function:

$$Z(T, V, N) = \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{h^3} \exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m}\right]$$

identical
particles

phase space normalization
factor (Planck's const.)

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda(T)^3}\right)^N$$

where $\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$

The length scale $\lambda(T)$ will turn out to control the onset of quantum effects in the ideal gas.

Free Energy:

$$F = -k_B T \ln Z$$

$$\Rightarrow = -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3N}{2} k_B T \ln \left(\frac{2\pi m k_B T}{h^3}\right)$$

$$F = -N k_B T \left[\ln \left(\frac{V e}{N}\right) + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2}\right) \right]$$

$$dF = -SdT - PdV + \mu dN$$

$$\rightarrow S = -\left. \frac{\partial F}{\partial T} \right|_{V, N}$$

$$= Nk_B \left[\ln\left(\frac{Vc}{N}\right) + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right) \right] + Nk_B T \cdot \frac{3}{2T}$$

$$S = -\frac{F}{T} + \frac{3}{2} Nk_B$$

$$F = E - TS \rightarrow S = -\frac{F}{T} + \frac{E}{T}$$

$$\Rightarrow E = \frac{3}{2} Nk_B T$$

Equation of State:

$$P = -\left. \frac{\partial F}{\partial V} \right|_{T, N} = \frac{Nk_B T}{V}$$

$$\Rightarrow PV = Nk_B T$$

Chemical Potential:

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T, V} = \frac{E}{N} + k_B T \left(= \frac{E - TS + PV}{N} \right)$$

$k_B T = \frac{PV}{N}$

$$\mu = k_B T \ln\left(\frac{N \lambda^3}{J}\right)$$

one-particle probability distribution:

$$P(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{p_1^2}{2m k_B T}\right)$$

Maxwell-Boltzmann