Meet the Ensembles

MSE 421 - Ceriotti

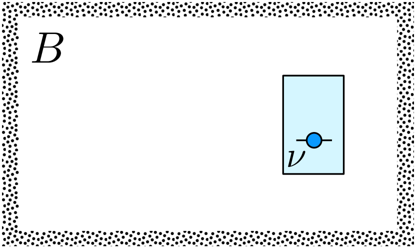
The canonical (constant-T) ensemble/1

- Imagine a system coupled to a bath, and assume we know the density of states for a large bath, $\Omega_B(E)$. The system+bath system is kept at constant energy E and the subsystem is *in a defined state* with energy E_ν.
  - The number of states of the bath is going to be $\Omega_B(E - E_\nu)$
  - We can expand $\ln \Omega_B$ as a Taylor series

$$\ln \Omega_B(E - E_\nu) = \ln \Omega_B(E) - E_\nu \frac{\partial \ln \Omega_B(E)}{\partial E} + \ldots$$

  - This gives us the probability of a state given its energy $[\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln \Omega}{\partial E}]$

$$P_\nu(E_\nu) \propto \Omega_B(E - E_\nu) \propto \exp - E_\nu \frac{\partial \ln \Omega_B(E)}{\partial E} = \exp - \frac{E_\nu}{k_B T}$$



The Partition Function/1

- Note that P_ν is computed *for a single state*. If degenerate states with the same energy are present, they have to be counted separately, i.e.

$$P(E) \propto \Omega(E)\, e^{-E/k_BT}$$

- The normalization constant is the so-called **partition function**

$$P_\nu = \frac{e^{-E_\nu/k_BT}}{Q} = \frac{e^{-E_\nu/k_BT}}{\sum_{\nu'} e^{-E_{\nu'}/k_BT}}$$

  - For discrete states, Q is a sum over states [QM: no need to know energy eigenstates: $Q = \sum_\nu \langle\nu|\, e^{-\beta\hat{H}}\, |\nu\rangle = \mathrm{Tr}\, e^{-\beta\hat{H}}$ can be evaluated over any complete basis]

$$\text{QM: } Q(N,V,T) = \sum_\nu e^{-E_\nu/k_BT}$$

  - Classically, the probability involve a density and so Q is an integral over phase space [The partition function is the Laplace transform of the density of states Ω, so it has the same content of information $Q(N,V,\beta) = \int \Omega(E,N,V)\, e^{-\beta E} \mathrm{d}E$]

$$\text{CL: } Q(N,V,T) = \int e^{-E(\mathbf{q},\mathbf{p})/k_BT} \mathrm{d}\mathbf{p}\mathrm{d}\mathbf{q}$$

The Partition Function/2

- The partition function contains a great deal of information about thermodynamics
  - The internal energy can be obtained from

$$-\frac{\partial \ln Q}{\partial \beta} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = \sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{Q} = \langle E \rangle$$

  - One can also get energy fluctuations

$$-\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial^2 \ln Q}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{Q} = \sum_\nu E_\nu^2 \frac{e^{-\beta E_\nu}}{Q} + \sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{Q^2}\frac{\partial Q}{\partial \beta} =$$

$$= \sum_\nu E_\nu^2 \frac{e^{-\beta E_\nu}}{Q} + \frac{1}{Q}\frac{\partial Q}{\partial \beta}\sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{Q} = \left\langle E^2 \right\rangle - \langle E \rangle^2 = \mathrm{var}\,(E)$$

  - Fluctuations become negligible in the thermodynamic limit!

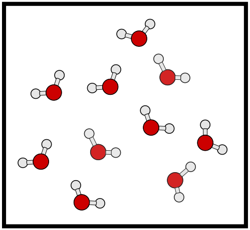
$$-\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial \langle E \rangle}{\partial T}\frac{\partial T}{\partial \beta} = C_V T^2 k_B \sim \mathcal{O}(N)$$

$$\frac{\sigma(E)}{\langle E \rangle} \sim \frac{\sqrt{\mathcal{O}(N)}}{\mathcal{O}(N)} = \frac{1}{\sqrt{\mathcal{O}(N)}} \xrightarrow[N\to\infty]{} 0$$

Ideal gas

- What's the partition function for an ideal gas with N atoms in a volume V?
  $Q = \int e^{-\sum_i \mathbf{p}_i^2/2mk_BT} d\mathbf{p}^N d\mathbf{q}^N / N!$ to avoid counting indistinguishable state
- The integral is easily evaluated to $Q = \left[(m\pi/\beta)^{3/2}\left(2\sqrt{2}V\right)\right]^N / N!$, so
  $\ln Q = N\left[1 + \frac{3}{2}\ln\frac{m\pi}{\beta} + \ln V + \frac{1}{2}\ln 8\right] - N\ln N$
- For instance one can compute the average energy and heat capacity

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Q = \frac{3N}{2\beta} = \frac{3N}{2}k_BT, \qquad C_V = \frac{3N}{2}k_B$$



A two-state system

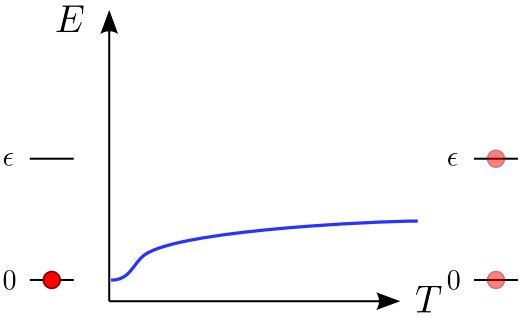
- Consider a quantum system that can exist in two states, with energies 0 and ϵ.

$$Q = e^0 + e^{-\beta\epsilon} = 1 + e^{-\beta\epsilon}$$

- Average energy

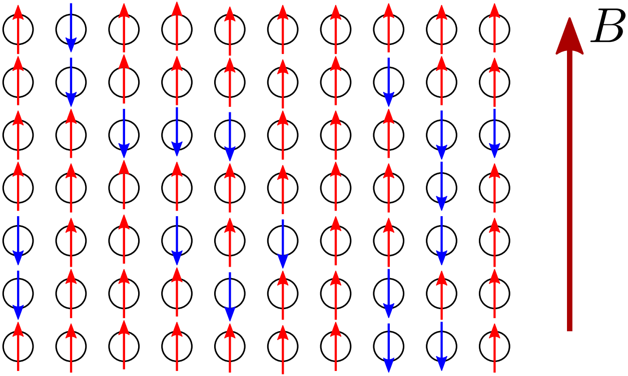
$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Q = -\epsilon\frac{-e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon}+1}$$

$$T\to 0, \langle E\rangle \to 0, T\to\infty, \langle E\rangle\to \epsilon/2$$



A paramagnetic material

- Consider a large number *N* of independent spins in a magnetic field.
- Each can have two energy levels, $\epsilon = \mu B$ and $-\epsilon = -\mu B$.
- What is the energy, and the magnetization, as a function of temperature?



Non-interacting spins - microcanonical

- What is the (microcanonical) density of states?
  - Given m spins in the "up" state, the internal energy is $[x = E/N\epsilon]$

$$E = -m\epsilon + (N-m)\,\epsilon = (N-2m)\,\epsilon \qquad \rightarrow m = \frac{1}{2}\left(N - \frac{E}{\epsilon}\right) = \frac{N}{2}\,(1-x)$$

  - The number of ways to arrange m spins "up" and $N-m$ spins "down" is

$$\Omega = \frac{N!}{m!\,(N-m)!} \approx e^{N\ln N - m\ln m - (N-m)\ln(N-m)} = e^{N\ln N - m\ln m - (N-m)\ln(N-m)}$$

$$\ln\Omega\,(E) = N\,(\ln N + \ln 2) - \frac{1}{2}\left[\left(N - \frac{E}{\epsilon}\right)\ln\left(N - \frac{E}{\epsilon}\right) + \left(N + \frac{E}{\epsilon}\right)\ln\left(N + \frac{E}{\epsilon}\right)\right]$$

  - What is the (inverse) temperature for a given energy/number of "up" spins?

$$\beta = \frac{\partial\ln\Omega}{\partial E} = -\frac{1}{2\epsilon}\left[-1 - \ln\left(N - \frac{E}{\epsilon}\right) + 1 + \ln\left(N + \frac{E}{\epsilon}\right)\right] = \frac{1}{2\epsilon}\ln\frac{1 - \frac{E}{N\epsilon}}{1 + \frac{E}{N\epsilon}}$$

  - We can invert the relation to obtain E as a function of β

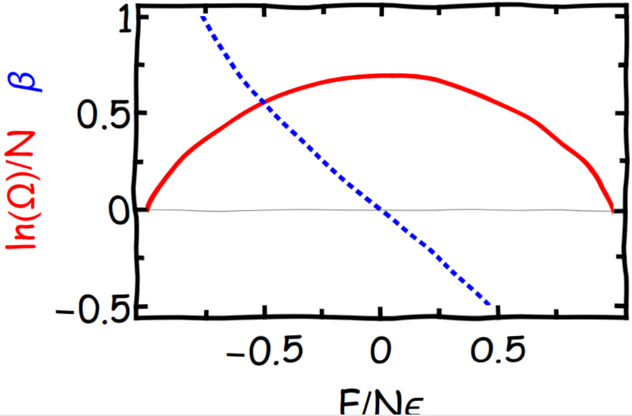
$$\frac{1 - \frac{E}{N\epsilon}}{1 + \frac{E}{N\epsilon}} = e^{2\beta\epsilon} \qquad \rightarrow \qquad \frac{E}{N\epsilon} = \frac{1 - e^{2\beta\epsilon}}{1 + e^{2\beta\epsilon}} = \frac{e^{-\beta\epsilon} - e^{\beta\epsilon}}{e^{\beta\epsilon} + e^{-\beta\epsilon}}$$

Negative temperature?

- Summarizing the microcanonical versions of density of states and inverse temperature. . .

$$\ln \Omega(E) = N(\ln N + \ln 2) - \frac{1}{2}\left[\left(N - \frac{E}{\epsilon}\right)\ln\left(N - \frac{E}{\epsilon}\right) + \left(N + \frac{E}{\epsilon}\right)\ln\left(N + \frac{E}{\epsilon}\right)\right]$$

$$\beta = \frac{\partial \ln \Omega}{\partial E} = -\frac{1}{2\epsilon}\left[-\ln\left(N - \frac{E}{\epsilon}\right) + \ln\left(N + \frac{E}{\epsilon}\right)\right] = \frac{1}{2\epsilon}\ln\frac{1 - \frac{E}{N\epsilon}}{1 + \frac{E}{N\epsilon}}$$



Non-interacting spins - canonical

- The canonical partition function can be written as a sum over energy levels

$$Q = \sum_{m=0}^{N} \frac{N!}{m!\,(N-m)!} e^{-\beta(N-2m)\epsilon} = \sum_{E} e^{-\beta E}\Omega(E)$$

- General result: given two non-interacting systems, the overall partition function is the product of the two partition functions

$$Q_1 = \sum_{\nu_1} e^{-\beta E_{\nu_1}}, \quad Q_2 = \sum_{\nu_2} e^{-\beta E_{\nu_2}} \quad \rightarrow \quad Q = \sum_{\nu_1,\nu_2} e^{-\beta\left(E_{\nu_1}+E_{\nu_2}\right)} = Q_1 Q_2$$

- Each of the N spins can exist in two states.

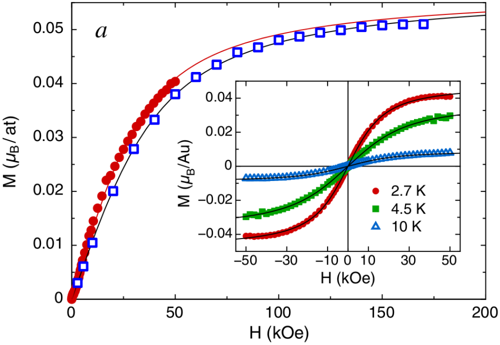
$$Q_1 = e^{-\beta\epsilon} + e^{\beta\epsilon}, \qquad Q = Q_1^N$$

- Simple to see: $E(\beta)$ matches the microcanonical case

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = -N\frac{\partial \ln Q_1}{\partial \beta} = -N\epsilon\frac{-e^{-\beta\epsilon}+e^{\beta\epsilon}}{e^{-\beta\epsilon}+e^{\beta\epsilon}} = N\epsilon\frac{e^{-\beta\epsilon}-e^{\beta\epsilon}}{e^{\beta\epsilon}+e^{-\beta\epsilon}}$$

How about magnetization?

- For a system with m spins "up", the magnetization is just $M = \mu m - \mu(N-m) = -\frac{\mu}{\epsilon}E$
$$\frac{\langle M\rangle}{N} = -\mu\frac{e^{-\beta\epsilon}-e^{\beta\epsilon}}{e^{\beta\epsilon}+e^{-\beta\epsilon}} = -\mu\tanh -\beta\epsilon = \mu\tanh\beta\mu B$$
- For small values of the applied field, one obtains Curie's law
$$\frac{M}{N} \approx \frac{\mu^2 B}{k_B T}$$



Paramagnetism of gold nanoparticles (Bartolomé et al., PRL 2012)