Canonical Ensemble, Continued

Reminder....

$$Z = \int dX \, e^{-\beta \mathcal{H}(X)} \quad , \; \beta = 1/k_B T$$

$$\langle \mathcal{E} \rangle = -\frac{\partial \log Z}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} Z$$

also $\dfrac{\partial f}{\partial x} = \dfrac{\partial f}{\partial \beta} \partial\beta/\partial x \Rightarrow \dfrac{\partial f}{\partial T} = \dfrac{\partial f}{\partial \beta} \dfrac{\partial (1/k_B T)}{\partial T}$

$$= -1/k_B T^2 \, \partial f/\partial \beta$$

$$\Rightarrow \frac{\partial f}{\partial T} = -\beta/T \, \partial f/\partial \beta$$

Now, how do we get thermodynamic quantities from this?

$$A(N,V,T) = \mathcal{E} - TS = \mathcal{E} + T\frac{\partial A}{\partial T}$$

(from $S = -\partial A/\partial T$) earlier

Replace $\mathcal{E}$ w/ $\langle \mathcal{E} \rangle = -\dfrac{\partial \log Z}{\partial \beta} = k_B T^2 \dfrac{\partial \log Z}{\partial T}$

or $-\partial \log Q/\partial \beta$

So $A = -\frac{\partial \log Q}{\partial \beta} - \beta \frac{\partial A}{\partial \beta}$

it turns out the solution to this is

$$\boxed{A = -\frac{1}{\beta} \log Q = -k_B T \log Q}$$

we can check this, $\frac{\partial A}{\partial \beta} = (-1/\beta) \frac{\partial \log Q}{\partial \beta} + \frac{1}{\beta^2} \log Q$

$\Rightarrow \beta \, \partial A/\partial\beta = -\partial \log Q/\partial \beta - A$

$\Rightarrow A = -\partial \log Q/\partial\beta - \beta \, \partial A/\partial \beta$ ✓

So, now log partition func is $\propto$ free energy instead of entropy

Other quantities we want -

$S = -\partial A/\partial T = + k \log Q + kT \frac{\partial \log Q}{\partial T}$

$P = -\partial A/\partial V = + kT \frac{\partial \log Q}{\partial V}$

$\mu = \partial A/\partial N = -kT \, \partial \log Q/\partial N$

$\mathcal{E} = A + TS = (-kT \log Q) + T\,(k \log Q + kT\, \partial \log Q/\partial T)$

$= kT^2 \, \partial \log Q/\partial T = -\partial \log Q/\partial\beta$ (already showed)

Last $C_v = (\partial \mathcal{E}/\partial T)_{N,V} = -kT^2 \left(\frac{\partial \mathcal{E}}{\partial \beta}\right)_{N,V} = +kT^2 \frac{\partial^2 \log Q}{\partial \beta^2}$

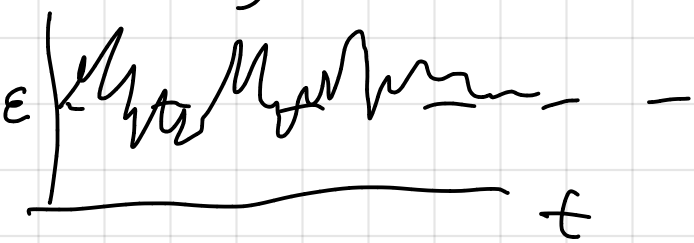
heat capacity const volume

$= k\beta^2 \, \partial^2 \log Q/\partial \beta^2$

$$\langle \mathcal{E} \rangle = -\frac{\partial}{\partial \beta} \log Q(N,V,T)$$

In the microcanonical ensemble, the energy is perfectly conserved. In canonical ensemble, the energy must fluctuate around $\langle \mathcal{E} \rangle$

eg.



We can quantify the size of these fluctuations by computing the variance or mean square fluctuation (MSF)

$$\langle (\delta \mathcal{E})^2 \rangle = \langle (\mathcal{E} - \langle \mathcal{E} \rangle)^2 \rangle = \langle \mathcal{E}^2 \rangle - \langle \mathcal{E} \rangle^2$$

The second term is clearly $\left(\frac{\partial \log Z}{\partial \beta}\right)^2 = \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2$

The first term is $\frac{1}{Z}\int dx\, e^{-\beta \mathcal{H}(x)} \mathcal{H}(x)^2$

and this term is $\frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z$

$$\text{so MSF} = \frac{1}{Z}\frac{\partial^2}{\partial \beta^2} Z - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

but $\underbrace{\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)}_{\downarrow} = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{1}{Z^2}\frac{\partial Z}{\partial\beta}\right)\frac{\partial Z}{\partial\beta} = MSF$

$$\frac{\partial^2 \log Z}{\partial\beta^2} = C_V/k_B\beta^2 = k_B T^2 C_V$$

$C_V = \frac{\partial E}{\partial T} = \frac{1}{k_B T^2}\,\mathrm{Var}(E)$, variance of E directly related to heat capacity

this is an example of a fluctuation-dissipation theorem, a fundamental part of non eq stat mech and spectroscopy (linear response theorem)

(cf. Eric's senior thesis)

we will discuss this more later in the semester

Now, how big are the energy flucts compared to the mean

$$\frac{\sqrt{\langle \delta E^2\rangle}}{E} \propto \frac{\sqrt{C_V}}{E} \propto \sqrt{N}/N \propto 1/\sqrt{N}$$

discussed this in first lecture,

fluctuations in thermo quantities small compared to mean in thermo limit!

Canonical ensemble, examples

1 and N particles in a box (much easier then microcanonical)

First,  $\mathcal{H} = p^2/2m$ "V" = L

$$q = \frac{1}{h} \cdot \int_0^L dq \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m} = \frac{L}{h} \cdot \sqrt{\frac{\pi}{a}} = \frac{L}{h}\sqrt{2\pi m k_B T} \quad ✓$$

$$\text{"}a\text{"} = \frac{1}{2mkT} \qquad = L/\Lambda$$

N particles in a box

$$Q = \frac{1}{h^{3N} N!} \int dq^{3N} \int dp^{3N} e^{-\beta \sum p_i^2/2m}$$

← already did something like this in HW

$$= \frac{1}{h^{3N} N!} L^{3N} \cdot (2\pi m k_B T)^{3N/2}$$

$$= \frac{1}{N!} V^N / \Lambda^{3N}$$

$$P = kT \frac{\partial}{\partial V} \log Q = kTN \frac{\partial}{\partial V}(\log V + \text{"const"})$$

$$= kTN/V$$

$$\Rightarrow \boxed{PV = N k_B T}$$

$$E = -\partial \log Q / \partial \beta = + \frac{\partial}{\partial \beta} 3N \log\left(\frac{h^2}{2\pi m}\beta\right)$$

$$= + \frac{\partial}{\partial \beta} \frac{3N}{2}(\log \beta + \text{const})$$

$$= + \partial/\partial\beta\ 3N/2 \log \beta = \frac{3 N k_B T}{2} \quad ✓$$

Harmonic Oscillator @ temp T

$\swarrow \omega = \sqrt{k/m}$

$$\mathcal{H} = p^2/2m + \tfrac{1}{2} k q^2 = p^2/2m + \tfrac{1}{2} m \omega^2 q^2$$

1 particle, no real volume, so write

$$Q(\beta) = \frac{1}{h} \int dp\, dq\, e^{-\beta(p^2/2m + \frac{1}{2} m\omega^2 q^2)}$$

$$= 1/h \left(\frac{2\pi m}{\beta}\right)^{1/2} \cdot \left(\frac{1}{\beta} \frac{2\pi}{m\omega^2}\right)^{1/2}$$

$\Leftarrow$ book missing β

$$= \frac{2\pi}{\beta h \omega} = \frac{1}{\beta \hbar \omega}$$

$$\mathcal{E} = -\frac{\partial \log Q}{\partial \beta} = +\frac{\partial \log \beta}{\partial \beta} = k_B T$$

(avg pot or KE $= k_B T/2$)

$$C = d\mathcal{E}/\partial T = k_B$$

N oscillators,

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2$$

distinguishable, and in 1d

$$Q(N,\beta) = \frac{1}{h^N} \int d\vec{p}^N d\vec{q}^N e^{-\beta H} = \prod_{i=1}^{N} q_i = \prod_{i=1}^{N} \frac{k_B T}{\hbar \omega_i}$$

$$\log Q(N,\beta) = \sum \log q_i$$

$$\mathcal{E} = -\sum \frac{\partial \log q_i}{\partial \beta} = N k_B T, \text{ and } C = N k_B$$