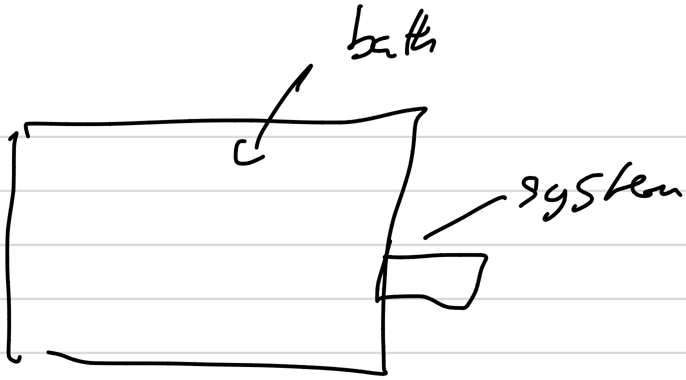
Lecture 6,

Canonical Ensemble continued



$$\mathcal{H}_{total} = \mathcal{H}_{sys} + \mathcal{H}_{bath}$$
$$\Rightarrow \mathcal{E}_{total} = \mathcal{E}_{sys} + \mathcal{E}_{bath}$$
$$S_{total} = S_{sys} + S_{bath}$$

$$S = k_B \log \Omega(N, V, \mathcal{E})$$

$$f(\vec{x}^{\,system}) \propto \Omega_b(N_b, V_b, \mathcal{E} - H_{sys})$$

$\mathcal{E} - \mathcal{E}_{bath}$ is small

$$S_{bath}(\mathcal{E}_b) \approx S_{bath}(\mathcal{E}) + \left(\frac{d}{d\mathcal{E}_b} S\right)\Bigg|_{\mathcal{E}=\mathcal{E}_{bath}} \overset{\sim -\mathcal{E}_{sys}}{(\mathcal{E}_b - \mathcal{E})} + \dots$$

$$\approx S_{bath}(\mathcal{E}) - \frac{1}{T}\mathcal{E}_{sys}$$

$$K \log \Omega_b(N_b, V_b, \mathcal{E}_b) \approx const - \mathcal{E}_{sys}/T$$

$$f(q,p) \propto \Omega_b(N_b, V_b, \mathcal{E}_b) = const \cdot e^{-\mathcal{E}_{sys}/k_B T}$$
$$\propto e^{-\mathcal{H}(\vec{x})/k_B T}$$

$$f(q,p) = e^{-\mathcal{H}(\vec{x})/k_B T}/Z, \qquad Z = \int d\vec{x}\, e^{-\beta \mathcal{H}(x)}$$

for N indistinguishable particles, often write

$$Q(N,V,T) = \frac{1}{h^{3N} N!} \int dp^{3N} dq^{3N} e^{-\beta \mathcal{H}(q,p)}$$

and $f(\vec{p},\vec{q}) = \frac{1}{h^{3N}N!} e^{-\beta \mathcal{H}(p,q)} / Q(N,V,T)$

cancels out $= e^{-\beta \mathcal{H}(p,q)} / Z(N,V,T)$ ✓

Now, how do we get thermodynamic quantities from this?

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

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

$$\langle E \rangle = \int dp\, dq\, \mathcal{H}(p,q) e^{-\beta \mathcal{H}(p,q)} \Big/ \int dp\, dq\, e^{-\beta \mathcal{H}(p,q)}$$

very important

$$= -\frac{\partial \log Z}{\partial \beta} = \frac{-\partial \log Q}{\partial \beta}$$

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

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

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

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

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

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 $C_V = (\partial \mathcal{E}/\partial T)_{N,V} = -\frac{1}{kT^2}\left(\frac{\partial \mathcal{E}}{\partial \beta}\right)_{N,V} = +\frac{1}{kT^2}\frac{\partial^2 \log Q}{\partial \beta^2}$

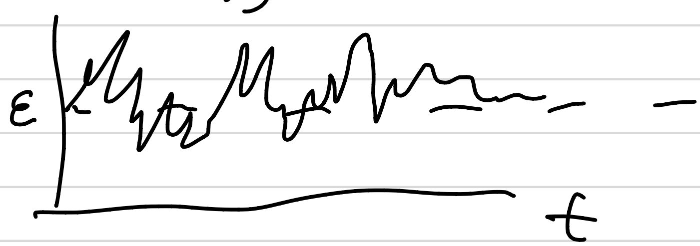
$$= k\beta^2\, \partial^2 \log Q/\partial \beta^2$$

heat capacity const volume

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

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 $\left(\frac{\partial \log Q}{\partial \beta}\right)^2 = \left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)^2$

The first term is $\frac{1}{h^{3N} N! \, Q_N} \int dx \, e^{-\beta \mathcal{H}(x)} \mathcal{H}(x)^2$

and this term is (remember homework probl)

$$\frac{1}{Q} \frac{\partial^2}{\partial \beta^2} Q$$

so $MSF = \frac{1}{Q}\frac{\partial^2}{\partial \beta^2} Q - \frac{1}{Q^2} \frac{\partial Q}{\partial \beta}$

but this $= \frac{\partial}{\partial \beta}\left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left(\frac{\partial \log Q}{\partial \beta}\right)$

$$= \frac{\partial^2}{\partial \beta^2}(\log Q) = \boxed{kT^2 \cdot C_v}$$

☆ $Var(E)$ is directly related to heat capacity

$$\partial E / \partial T = kT^2 \, Var(E)$$

is an example of a fluctuation-dissipation theorem, a fundamental part of non eq stat mech and spectroscopy (linear response theorem) we will discuss this more later in the semester

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

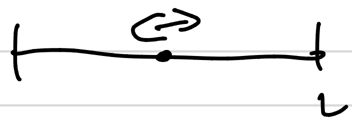
$$\frac{\sqrt{\langle \delta E^2 \rangle}}{E} = \frac{\sqrt{kT^2 C_V}}{E} \simeq \frac{\Delta E/E}{1} \qquad E \propto N \quad \text{and} \quad \underbrace{C_V}_{\left(\frac{\partial E}{\partial T}\right)_{N,V}} \propto N$$

$$\text{so} \quad \frac{\Delta E}{E} \sim \frac{\sqrt{N}}{N} \sim 1/\sqrt{N}$$

we talked about this in the first lecture, how bulk systems will have measured values extremely close to avg (and fluctuations will be seen for small systems)

Canonical ensemble, examples

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

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

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

"a" $= \frac{1}{2mkT}$

$$= L/\Lambda$$

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

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

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

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

$$= kTN/V$$

$$\Rightarrow \boxed{PV = Nk_BT}$$

$$E = -\partial \log Q / \partial\beta = -\frac{\partial}{\partial\beta} \frac{3N}{2}\left(\log \frac{1}{\beta} + \text{const}\right)$$

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

Harmonic Oscillator @ temp T

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

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

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

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

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

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

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 –

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

$\mathcal{E} = N k_B T$, and $C = N k_B$