Canonical Ensemble, Part II

$$Z = \int d\vec{x}\, e^{-\beta \mathcal{H}(\vec{x})} \qquad \beta = \frac{1}{k_B T}$$

$$\langle E \rangle = \int d\vec{x}\, E(\vec{x})\, P(\vec{x})$$

$$= \int d\vec{x}\, \mathcal{H}(\vec{x}) \left(\frac{e^{-\beta \mathcal{H}(\vec{x})}}{Z} \right)$$

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

$$\langle \varepsilon \rangle = -\frac{\partial \log Z}{\partial \beta} = +k_B T^2 \frac{\partial \log Z}{\partial T}$$

$$\frac{\partial f}{\partial x} = \left(\frac{\partial f}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial x}\right)$$

$$\left(\frac{\partial f}{\partial T}\right) = \left(\frac{\partial f}{\partial \beta}\right)\left(\frac{\partial (1/k_B T)}{\partial T}\right)$$

$$= -\frac{1}{k_B T^2}\left(\frac{\partial f}{\partial \beta}\right) = -\frac{\beta}{T}\left(\frac{\partial f}{\partial \beta}\right)$$

$$A(N,V,T) = \mathcal{E} - TS \qquad \left(S = -\frac{\partial A}{\partial T}\right)$$

$$= \langle \mathcal{E} \rangle + T\underbrace{\left(\frac{\partial A}{\partial T}\right)}$$

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

turns out: $A = -k_B T \log Z$

$$= -1/\beta \log Z$$

$$\boxed{A = -\frac{1}{\beta}\log Z}$$

$$\frac{\partial A}{\partial \beta} = \left(-\frac{1}{\beta}\right)\frac{\partial \log Z}{\partial \beta} + (\log Z)\left(\frac{\partial}{\partial \beta}\left(-\frac{1}{\beta}\right)\right)$$

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

$$\beta\frac{\partial A}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta} + \overbrace{\frac{1}{\beta}\log Z}^{-A}$$

$$A = -\frac{\partial \log Z}{\partial \beta} - \beta\frac{\partial A}{\partial \beta} \qquad \checkmark$$

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

$$S = -\left(\frac{\partial A}{\partial T}\right) = k_B \log Z + k_B T \frac{\partial \log Z}{\partial T}$$

$$P = -\frac{\partial A}{\partial V} = k_B T \frac{\partial \log Z}{\partial V}$$

$$\mu = \frac{\partial A}{\partial N} = -k_B T \frac{\partial \log Z}{\partial N}$$

$$\mathcal{E} = A + TS = -k_B T \log Z + T\left(\quad\right)$$
$$= k_B T^2 \, \partial \log Z / \partial T \ \checkmark$$

$$C_V = \left(\partial \mathcal{E}/\partial T\right)_{N,V}$$

(heat capacity for water 1 cal/g °C)

($\rho_{H_2O} \approx 1 g/mL = 1 kg/L$)

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

$$= +\frac{1}{k_B T^2}\frac{\partial^2 \log Z}{\partial \beta^2}$$

($\mathcal{E} = -\frac{\partial \log Z}{\partial \beta}$

$$= \boxed{k_B \beta^2 \, \partial^2 \log Z/\partial \beta^2}$$

$$\mathrm{Var}(\varepsilon) = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$$

$$\langle \varepsilon \rangle^2 = \left(- \frac{\partial \log Z}{\partial \beta} \right)^2 \qquad \left(Z = \int dx \, e^{-\beta H(x)} \right)$$

$$\langle \varepsilon^2 \rangle = \int dx \, (H(x))^2 \, ?(x) = \frac{1}{Z} \underline{\int dx \, H(x)^2 e^{-\beta H(x)}}$$

$$= \frac{1}{Z} \left(\frac{\partial}{\partial \beta} \left(\frac{\partial}{\partial \beta} Z \right) \right)$$

$$= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} (Z)$$

$$\mathrm{Var}(E) = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{\partial \log Z}{\partial \beta}\right)^2$$

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

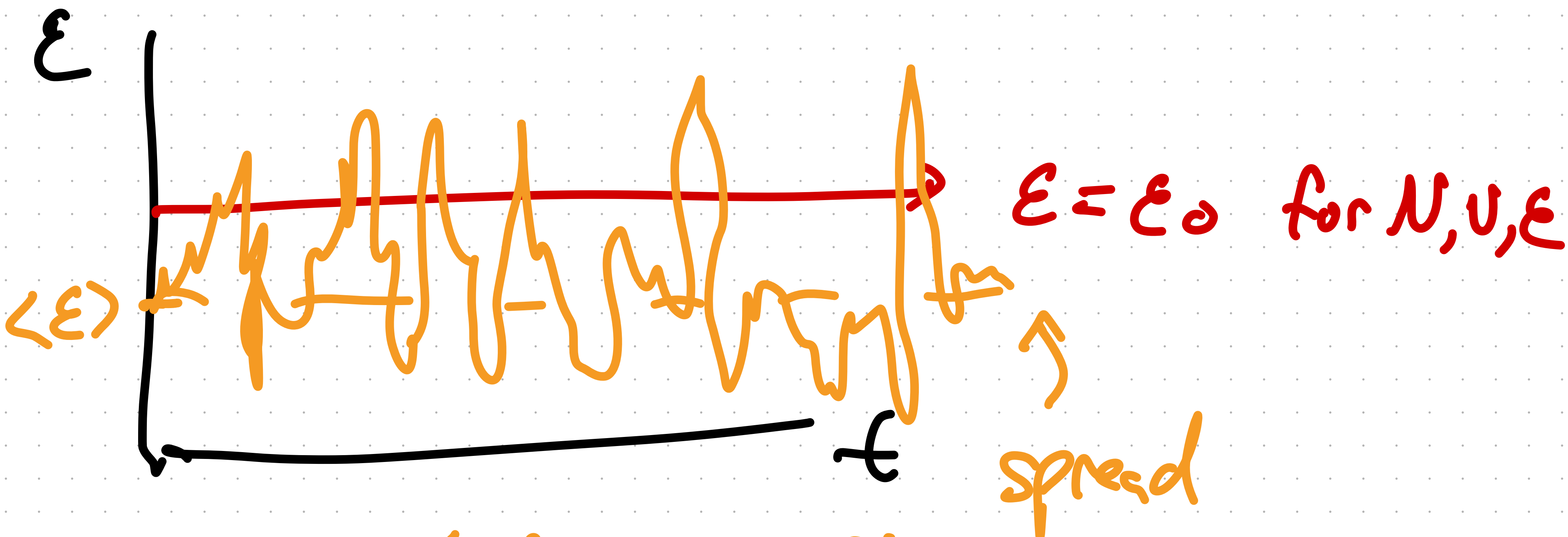
$$\underline{\frac{\partial^2}{\partial \beta}(\log Z)} = \frac{\partial}{\partial \beta}\left(\frac{\partial}{\partial \beta}\log Z\right) = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)$$

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

$$\left(C_V/_{k_B \beta^2}\right) = \mathrm{Var}(E)$$

$$\mathrm{Var}(\mathcal{E}) = \frac{C_v}{k_B \beta^2} = k_B T^2 C_V$$

$$C_v = \left(\frac{\partial \mathcal{E}}{\partial T}\right) = \frac{1}{k_B T^2} \mathrm{Var}(\mathcal{E})$$



$$\mathrm{Var}\,\mathcal{E} = \langle (\mathcal{E} - \langle \mathcal{E} \rangle)^2 \rangle$$

$$\frac{\partial A}{\partial x} \propto \mathrm{Var}(x)$$

"Onsager Regression Hypothesis"

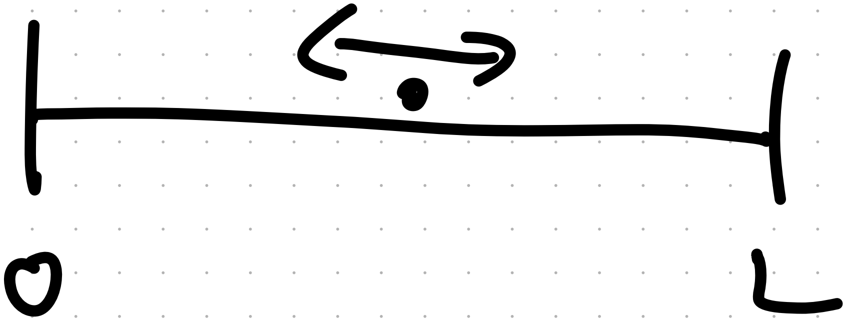
how big are the fluctuations?

$$\frac{\sqrt{\mathrm{Var}\,\varepsilon}}{\varepsilon} \propto \frac{\sqrt{C_v}}{\varepsilon} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}}$$

$$C_v = \frac{\partial \varepsilon}{\partial T} = \frac{\partial}{\partial T}(\varepsilon) \propto N$$

Examples

first :



$$\mathcal{H} = p^2/2m$$

$$q = \frac{1}{h}\int_0^L dx \int_{-\infty}^{\infty} dp\, e^{-\beta \mathcal{H}(p)} = \frac{L}{h}\int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m}$$

$\sqrt{\pi/a}$

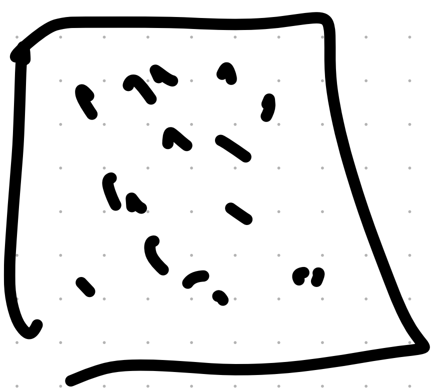
$a = \beta/2m$

$$= \frac{L}{h}\sqrt{2\pi m k_B T}$$

N particles in a box

$$\mathcal{H} = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m = \sum_{i=1}^{3N} p_i^2/2m$$

$$Q = \frac{1}{h^{3N} N!} \int_0^L dx^{3N} \underbrace{\int dp^{3N} e^{-\beta \mathcal{H}(x)}}$$



$$\int dp^{3N} e^{-\beta \sum p_i^2/2m}$$

$$=$$

$$\int dp_1 e^{-\beta p_1^2/2m} \cdot \int dp_2 e^{-\beta p_2^2/2m} \cdots$$

$$Q = \frac{1}{N!}\left[\frac{1}{h}\int_0^L dx \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m}\right]^{3N}$$

$$= \frac{1}{N!}\, q_{1d}^{\,3N}$$

$$= \frac{L^{3N}}{N!}\left(\sqrt{\frac{2\pi m k_B T}{h^2}}\right)^{3N}$$

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

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \left(\frac{\partial (k_B T \log Q)}{\partial V}\right)_{N,T}$$

$$= k_B T \left(\frac{\partial \log Q}{\partial V}\right)_{N,T} \qquad Q = V^N \cdot (\ \ )$$

$$= k_B T \frac{\partial}{\partial V} \cdot \log(V^N)$$

$$= N k_B T / V$$

$$\Rightarrow \quad PV = N k_B T = nRT$$

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

$$= -\frac{\partial}{\partial \beta}\left[\log\left(\frac{1}{\beta^{3N/2}}\right)\right]$$

$$= \frac{\partial}{\partial \beta}\left(\frac{3N}{2} \log \beta\right)$$

$$= \frac{3N}{2} \cdot \frac{1}{\beta} = \frac{3}{2} N k_B T \checkmark$$

$$= 3/2\, nRT$$

$$\partial \mathcal{E}/\partial T = 3/2\, nR = C_V$$

Harmonic Oscillator

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

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

$$= p^2/2m + \frac{1}{2} m \omega^2 x^2$$

$$Q(\beta) = \frac{1}{h} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \, e^{-\beta (p^2/2m)} \, e^{-\beta \frac{1}{2} m \omega^2 x^2}$$

β missing in book

$$= \frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \cdot \sqrt{\frac{2\pi}{m\omega^2 \beta}} = \frac{2\pi}{\beta h \omega} = \frac{1}{\beta \hbar \omega}$$

$$Q = \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega}$$

$\log \frac{1}{\beta\hbar\omega}$
$= -\log\beta$
$-\log\hbar\omega$

$$\mathcal{E} = -\frac{\partial \log Q}{\partial \beta} = \frac{-\partial \log\left(\frac{1}{\beta\hbar\omega}\right)}{\partial \beta}$$

$$= \frac{1}{\beta} = k_B T$$

avg pot $\frac{k_B T}{2}$

avg kin $\frac{k_B T}{2}$

$$C_V = \frac{\partial \mathcal{E}}{\partial T} = k_B$$

N oscillators, freq ω_i

$$\mathcal{H} = \sum_{i=1}^{N} p_i^2/2m + \frac{m\omega_i^2}{2} x^2$$

$$Q = \frac{1}{h^N} \int dp^N \int dq^N e^{-\beta \mathcal{H}}$$

$$= \left(\frac{1}{h} \int dp \int dq \, e^{-\beta \mathcal{H}_1} \right)^N = \prod_{i=1}^{N} q_i$$

$$q_i = \frac{k_B T}{\hbar \omega_i}$$

$$\log Q = \log (q_1 q_2 \cdots q_N)$$

$$= \sum \log q_i$$

$$E = \sum \varepsilon_i = N k_B T$$

$$C_V = N k_B$$