Key concept in Stat. Mech. → Thermodynamic properties can exhibit fluctuations around their mean value.

→ what is their magnitude?
→ Consequences on behavior?

$$P_m = \frac{e^{-\beta E_m}}{Q(T,V,N)} \quad \text{in canonical } (N,V,T) \text{ ensemble}$$

$$\langle X \rangle = \sum_{\substack{\text{all states}\\ \text{at } N,V}} X_m P_m \quad \leftarrow \text{average value of } X$$

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle$$

$$= \langle x^2 \rangle - 2\langle x \rangle\langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\Rightarrow \sigma_x^2 = \sum P_m X_m^2 - \left(\sum P_m X_m \right)^2$$

Energy distribution and fluctuations

$$P(E) = \sum_m P_m \delta_{E_m,E} = \sum_m \frac{e^{-\beta E_m}}{Q(T,V,N)} \delta_{E_m,E} =$$

$$= \frac{\Omega(E,V,N)\, e^{-\beta E}}{Q(T,V,N)}$$

Q can also be written as a summation over energies (rather than microstates):

$$Q = \sum_{\text{all } E_i} \Omega(E_i,V,N)\, e^{-\beta E_i} \qquad E_i: \text{energy levels}$$

Operation on partition function is a Laplace Transform (microscopic analog of Legendre transform)

Fluctuations: $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \sum_{\substack{\text{microstates} \\ m \text{ at } V,N}} P_m E_m^2 - \left(\sum_m P_m E_m \right)^2$

$$Q = \sum_m e^{-\beta E_m} ; \quad P_m = e^{-\beta E_m}/Q$$

$$\left.\frac{\partial Q}{\partial \beta}\right)_{V,N} = -\sum_m E_m e^{-\beta E_m} = -Q \sum_m P_m E_m$$

$$\left.\frac{\partial^2 Q}{\partial \beta^2}\right)_{V,N} = \sum_m E_m^2 e^{-\beta E_m} = Q \sum_m P_m E_m^2$$

$$\sigma_E^2 = \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} - \left[\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right]^2 = \frac{\partial^2 \ln Q}{\partial \beta^2} = -\left.\frac{\partial \langle E \rangle}{\partial \beta}\right)_{V,N}$$

$\therefore$ Fluctuations are proportional to the second derivative of the ln[relevant partition function] (thermodynamic potential)

$\ln \Omega = \frac{S}{k_B} = y^{(0)} \qquad d\ln \Omega = \beta\, dE + \beta P\, dV - \beta\mu\, dN$

$\ln Q = -\frac{A}{k_B T} = y^{(1)} \qquad d\ln Q = -E\, d\beta + \beta P\, dV - \beta\mu\, dN$

$$\sigma_E^2 = \langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Q}{\partial \beta^2} = -\frac{\partial E}{\partial \beta} = \underline{\underline{k_B T^2 C_V}}$$

The mean-square fluctuation of E is proportional to the heat capacity at const. volume.

Relative magnitude $\frac{\sqrt{\sigma_E^2}}{E} = \frac{\sqrt{C_V k_B T^2}}{E} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$

Relative fluctuations go down as $\sqrt{N}$

$N \simeq 1000$ (simulations) $\frac{\sqrt{\sigma_E^2}}{E} \sim 3\%$

$N \simeq 10^{23}$ (lab) $\sim 10^{-11}$

The relationship $\sigma_E^2 = \left.\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,N}$ for $\langle E^2\rangle - \langle E\rangle^2$ in the NVT ensemble can be readily generalized to <u>any</u> ensemble -

Eg. grand Canonical (μVT) ensemble:

$$\langle N^2\rangle - \langle N\rangle^2 = \sigma_N^2 = \left(\frac{\partial^2 \ln \Xi}{\partial(\beta\mu)^2}\right)_{\beta,V} = k_B T \left[\frac{\partial\langle N\rangle}{\partial\mu}\right]_{T,V}$$

Constant-pressure (NPT) ensemble:

$$\langle V^2\rangle - \langle V\rangle^2 = \sigma_V^2 = \left.\frac{\partial^2 \ln \Delta}{\partial(\beta P)^2}\right)_{\beta,N} = -\left.\frac{\partial\langle V\rangle}{\partial(\beta P)}\right)_{\beta,N} = -k_B T \left.\frac{\partial\langle V\rangle}{\partial P}\right)_{T,N}$$

Note that these same derivatives in classical thermodynamics correspond to <u>stability conditions.</u> Near a limit of stability (or near a critical point) the corresponding fluctuations <u>diverge.</u>

These can even be generalized for cross-fluctuations, e.g. in μVT ensemble:

$$\langle \delta E\, \delta N\rangle = \langle (E-\langle E\rangle)(N-\langle N\rangle)\rangle = \langle EN\rangle - \langle E\rangle\langle N\rangle$$

$$= \frac{\partial^2 \ln \Xi}{\partial(\beta\mu)\partial\beta} = \left.\frac{\partial\langle N\rangle}{\partial\beta}\right)_{\mu,V} = -k_B T^2 \left.\frac{\partial\langle N\rangle}{\partial T}\right)_{\mu,V}$$