

Recap

$$Z = \sum_i e^{-\beta E_i}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\overline{(\Delta E)^2} = -\frac{\partial^2 \ln Z}{\partial \beta^2}$$

Suppose the system is characterized by a single external parameter x (Generalization to multiple parameters is trivial).

Consider a quasistatic change of the external parameter from x to $x+dx$. In this process the energy of the system in state r will change by the amount

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx, \quad dW_r = -dE_r$$

Macroscopic work dW done by the system as a result of change of x

$$dW = \frac{\sum e^{-\beta E_r} \left(-\frac{\partial E_r}{\partial x} dx \right)}{\sum e^{-\beta E_r}}$$

$$dW = \frac{\sum_r e^{-\beta E_r} \left(-\frac{\partial E_r}{\partial x} \right) dx}{\sum_r e^{-\beta E_r}}$$

$$\sum_r e^{-\beta \bar{E}_r} \frac{\partial E_r}{\partial x} = -\frac{1}{\beta} \frac{\partial}{\partial x} \left(\sum_r e^{-\beta E_r} \right) = -\frac{1}{\beta} \frac{\partial Z}{\partial x}$$

$$dW = \frac{1}{\beta Z} \frac{\partial Z}{\partial x} dx = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial x} \right) dx$$

$$dW = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} dx . \quad \text{---} \circledast$$

One can express dW in terms of the mean generalized force \bar{X}

$$dW = \bar{X} dx , \quad \bar{X} = - \overline{\frac{\partial E_r}{\partial x}}$$

Comparing with \circledast

$$\boxed{\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}}$$

for example $x = V$

$$dW = \bar{P} dV = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} dV$$

$$\boxed{F = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}} \quad Z(\beta, V)$$



Equation of state !! \bar{P} & T relations .

Connecting with Thermodynamics

Both \bar{E} and δW are expressible in terms of $\ln Z$.

→ should connect to Laws of Thermo

$Z(\beta, x)$, since $E_r = E_r(x)$.

$$d \ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta. \quad \text{**}$$

Consider a quasistatic process where β and x are changed so slowly so that system deviates from equilibrium only infinitesimally, hence the distribution is the canonical dist.

But we just showed

$$\frac{\partial \ln Z}{\partial x} dx = f dW \quad \text{and} \quad \bar{E} = - \frac{\partial \ln Z}{\partial \beta}.$$

Using these in $\ast \ast$

$$d \ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta .$$

$$= \beta dW - \bar{E} d\beta .$$

$$= \beta dW - d(\bar{E}\beta) + \beta d\bar{E}$$

$$d(\ln Z + \bar{E}\beta) = \beta dW + \beta d\bar{E}$$

$$\bar{E} = U$$

$$kT d(\ln Z + \beta \bar{E}) = d\bar{E} + dW \rightarrow$$

Identify with
Law of thermo

Identify $k(\ln Z + \beta \bar{E}) = S$

$$T dS = d\bar{E} + dW$$

$$\bar{E} = U .$$

$$S = k(\ln Z + \beta \bar{E})$$

$$TS = kT \ln Z + \bar{E}$$

Helmholtz potential $F = \bar{E} - TS .$

$$F = kT \ln Z$$

Recall we had .

$$\left(\frac{\partial F}{\partial T} \right)_V = -S$$

$$\bar{P} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \longleftrightarrow$$

$$\left(\frac{\partial F}{\partial V} \right)_T = -P .$$

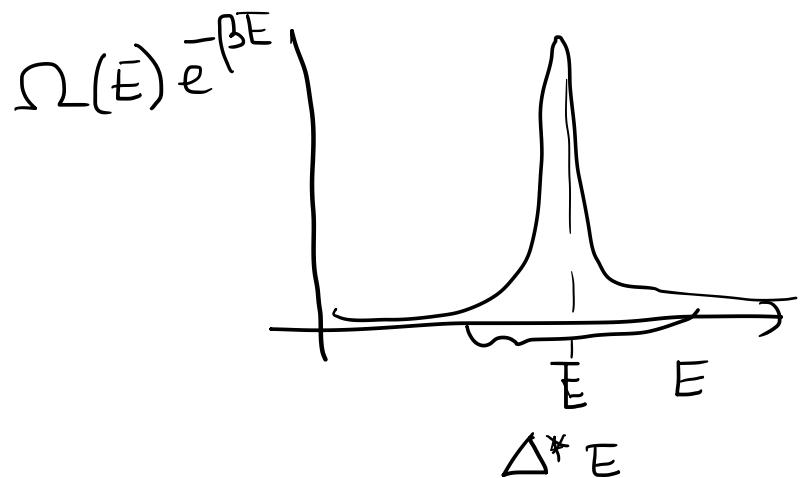
Q: How is this reconciled with our original defn.
of S in the microcanonical ensemble.

$$S = k \ln \Omega \xrightarrow{\# \text{ of microstates}}$$

$$S = k \ln Z + \beta \bar{E} \longrightarrow \text{canonical ensemble}$$

$\xrightarrow{\# \text{ of states between } E \text{ & } E + \delta E}$

$$Z = \sum_r e^{-\beta E_r} = \sum_E \underbrace{\Omega(E)}_{\text{rapidly growing}} e^{-\beta E}$$



$$Z \approx \Omega(\bar{E}) e^{-\beta \bar{E}} \left(\frac{\Delta^* E}{\delta E} \right)$$

$$\ln Z = \ln \Omega(\bar{E}) - \beta \bar{E} + \ln \underbrace{\frac{\Delta E^*}{\delta E}}_{\text{very small}}$$

at most f : f : # of degrees
of freedom

$$= \ln \Omega(\bar{E}) - \beta \bar{E} + \ln f$$

negligible

$$\Omega(\bar{E}) \sim \bar{E}^f$$

$$\simeq \ln \Omega(\bar{E}) - \beta \bar{E}$$

$$\boxed{\ln \Omega(\bar{E}) \approx \ln Z + \beta \bar{E}}$$