Chapter 3.4: Energy fluctuations

$$E = \langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\sum_r \varepsilon_r e^{-\beta \varepsilon_r} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$\Delta E^2 = \langle (\varepsilon - E)^2 \rangle = \langle \varepsilon^2 \rangle - E^2 = -\frac{\partial E}{\partial \beta}$$

Fluctuation-Dissipation relation

$$\langle \varepsilon^2 \rangle = \frac{1}{Z}\sum_r \varepsilon_r^2 e^{-\beta \varepsilon_r} = -\frac{1}{Z}\frac{\partial}{\partial \beta}\sum_r \varepsilon_r e^{-\beta \varepsilon_r} = -\frac{1}{Z}\frac{\partial}{\partial \beta}(ZE) = -\frac{1}{Z}\left(Z\frac{\partial E}{\partial \beta} + \frac{\partial Z}{\partial \beta}\cdot E\right)$$

$$= -\frac{\partial E}{\partial \beta} - \frac{1}{Z}\frac{\partial Z}{\partial \beta}\cdot E = -\frac{\partial E}{\partial \beta} + E^2$$

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

$$\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\Delta E^2 = -\frac{\partial E}{\partial \beta} = k_B T^2 \frac{\partial E}{\partial T} = k_B T^2 C_V$$

3.4-2 Energy fluctuations

Heat and work

$$dE = \delta Q + \delta W = TdS - \sum_\alpha F_\alpha d\alpha$$

$$E = \langle E \rangle = \sum_r P_r \langle r | \hat{H} | r \rangle = \sum_r P_r \varepsilon_r$$

$$dE = d\left(\sum_r P_r \varepsilon_r\right) = \underbrace{\sum_r \delta P_r \varepsilon_r}_{\delta Q} + \underbrace{\sum_r P_r \delta \varepsilon_r}_{\delta W}$$

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

$$\delta W = -\sum_\alpha F_\alpha d\alpha = \sum_\alpha \left(\frac{\partial E}{\partial \alpha}\right)_S d\alpha$$

$E = \sum_r P_r \varepsilon_r$

$$= \sum_\alpha \sum_r P_r \underbrace{\left(\frac{\partial \varepsilon_r}{\partial \alpha}\right) d\alpha}$$

$d\varepsilon_r = \sum_\alpha \left(\frac{\partial \varepsilon_r}{\partial \alpha}\right) d\alpha$

$$= \sum_r P_r d\varepsilon_r$$

Heat in the canonical ensemble

$$S = -k_B \sum_r P_r \ln P_r$$

$$d\ln P_r = \frac{dP_r}{P_r}$$

$$\sum_r dP_r \overset{!}{=} 0$$

$$\sum_r P_r = 1$$

$$dS = -k_B \sum_r d(P_r \ln P_r) = -k_B \sum_r (dP_r \ln P_r + P_r \, d\ln P_r)$$

$$= -k_B \sum_r \ln P_r \, dP_r - k_B \sum_r \cancel{\overset{1}{\frac{P_r}{P_r}} dP_r} \to 0$$

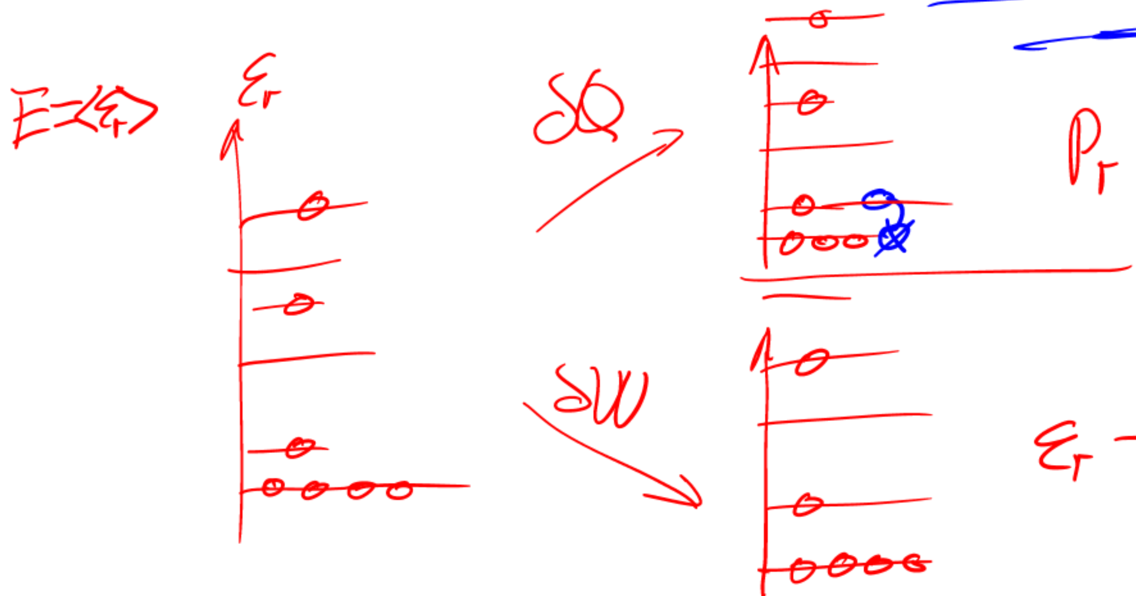
$$P_r = \frac{e^{-\beta\varepsilon_r}}{Z}$$

$$-\ln P_r = \ln Z + \beta\varepsilon_r$$

$$= k_B \sum_r (\ln Z + \beta\varepsilon_r) dP_r$$

$$= k_B \beta \sum_r \varepsilon_r dP_r = \frac{1}{T} \sum_r \varepsilon_r dP_r$$

$$\delta Q = TdS = \sum_r dP_r \varepsilon_r$$



$$P_r \to P_r + dP_r$$

$$\varepsilon_r \to \varepsilon_r + d\varepsilon_r$$