

Chapter 3.5: Energy fluctuations

$$E = \langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\Delta E^2 = \langle (\varepsilon - E)^2 \rangle = \langle \varepsilon^2 \rangle - E^2$$

$$\langle \varepsilon^2 \rangle = \frac{1}{Z} \sum_r \varepsilon_r^2 e^{-\beta \varepsilon_r}$$

3.5-2 Energy fluctuations

Heat and work

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

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

$$dE = d\left(\sum_r P_r \varepsilon_r\right) = \sum_r \delta P_r \varepsilon_r + \sum_r P_r \delta \varepsilon_r$$

3.5-3 Energy fluctuations

Heat in the canonical ensemble

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

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