Chapter 2.2: Entropy

We know: $dE = \delta Q + \delta W = TdS - \sum_\alpha F_\alpha d\alpha$ first law

Now: All thermodynamic variables are defined as expectation values or their derivatives.

$\hat{H}$ = Hamiltonian

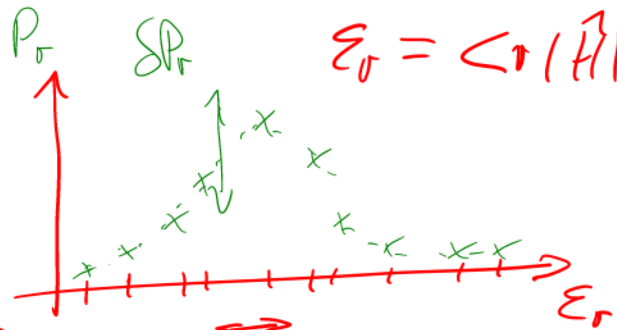
$$E = \langle E \rangle = \sum_r P_r \langle r|\hat{H}|r\rangle = \sum_r P_r \varepsilon_r$$

$|r\rangle$ not necessarily eigenstates of $\hat{H}$

$\varepsilon_r = \langle r|\hat{H}|r\rangle$ may not be spectrum

Hence:

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



1) change of $\delta\varepsilon_r = \sum_\alpha \langle r|\hat{H}(\alpha+d\alpha)-H(\alpha)|r\rangle$

$\leftrightarrow \delta\varepsilon_r$ by changing $\hat{H}$ depend on $\alpha = V, B, N, \ldots$

$$= \left(\frac{\partial \varepsilon_r}{\partial V}\right)_{P_r} dV + \left(\frac{\partial \varepsilon_r}{\partial B}\right) dB + \ldots$$

$$\sum_r P_r \delta\varepsilon_r = \left(\frac{\partial E}{\partial V}\right) dV + \left(\frac{\partial E}{\partial B}\right) dB + . = \sum_\alpha \left(\frac{\partial E}{\partial \alpha}\right) d\alpha = -\sum_\alpha F_\alpha d\alpha = \delta W$$

therefore 2.) $\sum_r \delta P_r \varepsilon_r = TdS$

Goal: A statistical definition of entropy

$S(P_r)$

Def. 2.6: The Entropy of a probability distribution P_r is defined as

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

Gibbs entropy formula

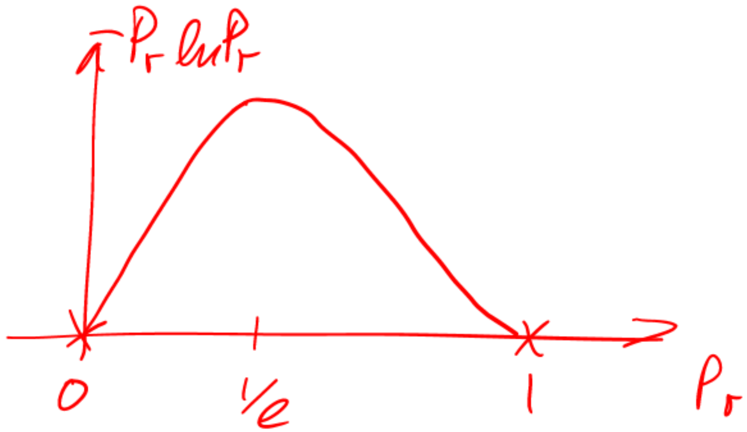
for information sciences
Shannon $S = -\sum_r P_r \ln P_r$

classically $S = -k_B \int d\Gamma\, P(\{\vec{r}_j, \vec{p}_j\}) \ln P(\{\vec{r}_j, \vec{p}_j\})$

von Neumann Entropy $S = -k_B \, \underline{\mathrm{tr}}(\hat{\rho} \ln \hat{\rho}) = -k_B \langle \ln \hat{\rho} \rangle$

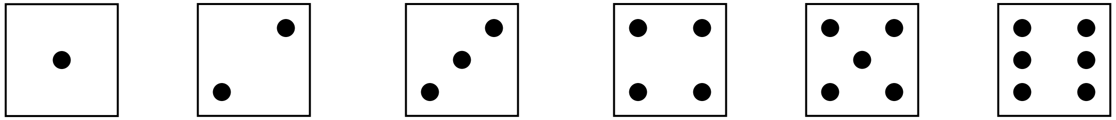
use $P_r = \langle r | \hat{\rho} | r \rangle$ in Eigenbasis

Claim: with this definition all thermodyn. laws can be derive.



$\mathrm{tr}\,\hat{\rho} = 1$

Example: Gambling



P_r	1/6	1/6	1/6	1/6	1/6	1/6
P_r	1/5	1/5	1/5	1/5	1/5	0
P_r	0	0	0	0	0	1

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

$$S = -k_B \sum_{r=1}^{6} \frac{1}{6} \ln \frac{1}{6} = k_B \ln 6$$

$$S = -k_B \sum_{r=1}^{5} \frac{1}{5} \ln \frac{1}{5} = k_B \ln 5 < \ln 6$$

$$S = 0$$

Any change from equal probabilities increases S

Max entropy $S = k_B \ln \Omega$

Ω = # of states

Example: two states

$r = 1 \quad P_1 = p$

$r = 2 \quad P_2 = (1-p)$

$$S = -k_B \left(p \ln p + (1-p) \ln(1-p) \right)$$