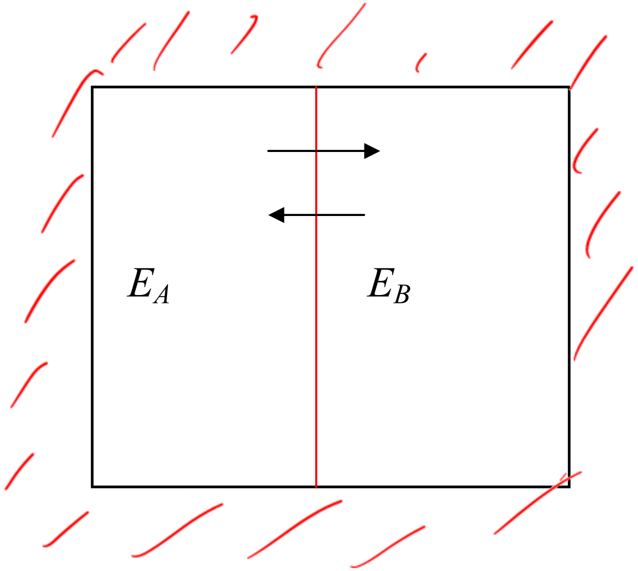
Chapter 3.1: Canonical Ensemble

energy fixed in large system

entropy $S(E, V, ..)$ calculated → thermodyn. potential

$$\beta = \frac{\partial \ln \Omega}{\partial E} \qquad p = T\left(\frac{\partial S}{\partial V}\right)_E$$

Derivation based on microcanonical ensemble



$$\delta S = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta E$$

$$\frac{\Omega_{\text{before}}}{\Omega_{\text{after}}} = e^{(\beta_A - \beta_B)\delta E}$$

idea: describe energy fluctuation probabilistically

also works for smaller systems at fixed T

what is probability for A to have energy E_A

E_tot conserved

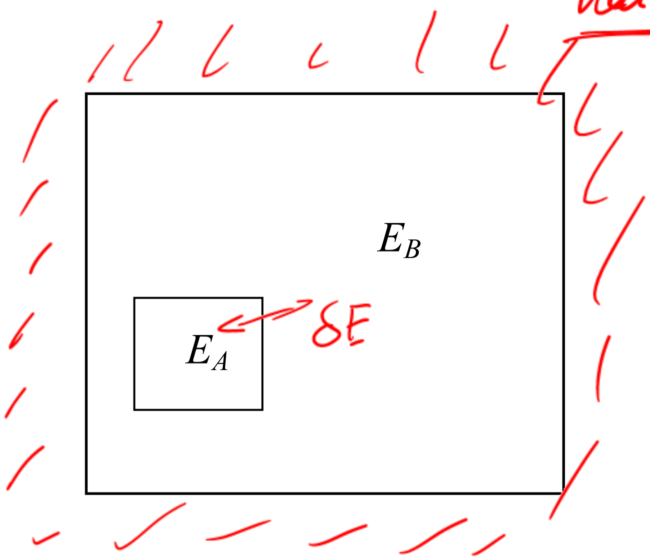
$E_B = E_{tot} - E_A$

Assumption: total system isolated and large (microcanonical) $\Omega_{tot}(E_{tot} = E_A + E_B)$

We are interested in a very small part A of the system (not isolated, $E_A << E_B$ not conserved)

part B has temperature T which is not affected by small changes δE

"heat bath" for system A



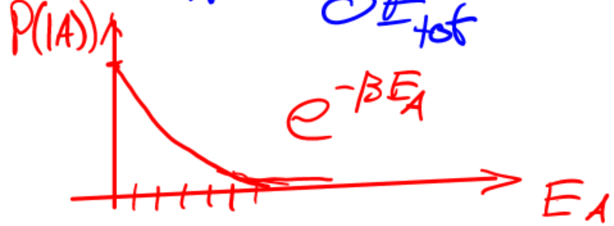
what is probability for system A to be in one particular microstate $|A\rangle$ with E_A

$\Omega_A(|A\rangle) = 1$ one state!

$$P(|A\rangle) = P(E_A) \propto \Omega_A(|A\rangle)\,\Omega_B(E_{tot} - E_A) = e^{\ln \Omega_B(E_{tot} - E_A)}$$

$$\ln \Omega_B(E_{tot} - E_A) \simeq \ln \Omega_B(E_{tot}) - E_A \frac{\partial \ln \Omega_B}{\partial E_{tot}} = \text{const} - \beta E_A$$

$$\underline{P(|A\rangle) \propto e^{-\beta E_A}}$$



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

Def. 3.1:

$|r\rangle$

The Boltzmann distribution $P_r = \frac{e^{-\beta\varepsilon_r}}{Z}$ is the probability of a microstate with energy ε_r, if the system is in contact with a heat bath of constant temperature $T = \frac{1}{k_B\beta}$.

The canonical partition function is $Z = \sum_r e^{-\beta\varepsilon_r}$ and gives normalization

$$1 = \sum_r P_r = \frac{\sum_r e^{-\beta\varepsilon_r}}{Z} \Rightarrow Z = \sum_r e^{-\beta\varepsilon_r}$$

classically $$Z = \int d\Gamma \, e^{-\beta \varepsilon(\{\vec{r}_j, \vec{p}_j\})}$$

Calculation of expectation values using the canonical ensemble

1.) Determine $Z = \sum_r e^{-\beta\varepsilon_r}$ and $P_r = \frac{e^{-\beta\varepsilon_r}}{Z}$

2.) Determine expectation values (and their derivatives)

e.g. $E = \langle \varepsilon \rangle = \sum_r P_r \varepsilon_r = \frac{\sum_r e^{-\beta\varepsilon_r}\varepsilon_r}{Z} = \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\underline{\underline{\sum_r e^{-\beta\varepsilon_r}}}\right) = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$

$= -\frac{\partial \ln Z}{\partial \beta}$

$\underline{\underline{S}} = -k_B \sum_r (P_r \ln P_r) = -\frac{k_B}{Z}\sum_r e^{-\beta\varepsilon_r} \ln \frac{e^{-\beta\varepsilon_r}}{Z} = -\frac{k_B}{Z}\sum_r e^{-\beta\varepsilon_r}(-\beta\varepsilon_r - \ln Z)$

$= k_B \beta E + k_B \ln Z = \underline{\underline{\frac{E}{T} + k_B \ln Z}}$

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

$\frac{1}{Z}\sum_r e^{-\beta\varepsilon_r} = 1$

$S = \frac{E}{T} + k_B \ln Z$

$F = E - TS$

$S = \frac{E}{T} - \frac{F}{T}$

Def. 3.2:
The Free Energy $F = E - TS$ is the thermodynamic potential of the canonical ensemble at given temperature $T = \frac{1}{k_B \beta}$. It can be calculated via

$$F = E - TS = E - T(k_B \ln Z + k_B \beta E) = -k_B T \ln Z(T, V, N, \alpha)$$

$$dF = dE - d(TS) = -S\,dT - p\,dV - \sum_\alpha F_\alpha \, d\alpha$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \qquad F_\alpha = -\left(\frac{\partial F}{\partial \alpha}\right)_{T,\text{rest}}$$

$F(T, V, \ldots)$ replaces $S(E, V, \ldots)$

* easier to calculate Z than Ω
* applies to small and large systems at fixed T
* energy not often conserved in many situations