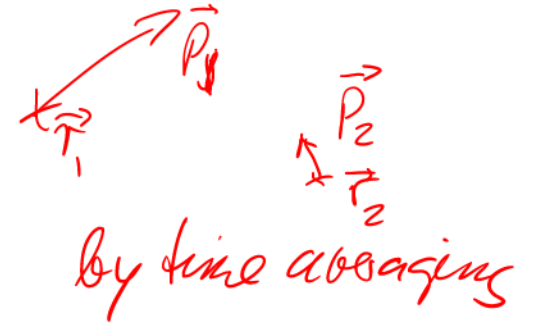


## Chapter 2.3: Microcanonical Ensemble

We use:  $S = -k_B \sum_r P_r \ln P_r$



Any restrictions increase the entropy. In equilibrium all states with equal energy are equally likely.

**Microcanonical Ensemble:** If the energy  $E$  is given, each Microstate with this energy must have the same probability in equilibrium. All other microstates have zero probability.

$$S = k_B \ln \Omega$$

$\Omega = \#$  of states with energy  $E$

$$P_r = \frac{1}{\Omega} \quad \text{if } \langle H \hat{r} | r \rangle = E$$

$$= 0 \quad \text{otherwise}$$

more general the energy must centered around  $E \pm \delta$

2.3-2 Microcanonical Ensemble

**Def. 2.6:** The total number of states  $\Omega(E, V, N, \dots)$  at a given energy  $E$  and other parameters  $V, N, \dots$  defines the Boltzmann entropy  $S = -k_B \sum_r P_r \ln P_r = \underline{k_B \ln \Omega}$ , which is the thermodynamic potential for the microcanonical ensemble.

$$S(E, V, N)$$

$P_r = \frac{1}{\Omega}$  for all microstates with energy  $E$ .

$$\Omega = \sum_r' \quad \text{with energy } E$$

$$\sum_r' P_r = \sum_r' \frac{1}{\Omega} = 1$$

how to calculate?

$$\Omega(E) \propto \int d\Gamma' \delta(E - \mathcal{E}(\vec{r}_j, \vec{p}_j)) \quad \left( \times \frac{1}{N!} \text{ due to over counting} \right)$$

$\mathcal{E}(\vec{r}_j, \vec{p}_j)$   
→ Gibbs factor

the overall prefactor depends dimensions, energy window, ... arbitrary.

quantum mechanics

$$\Omega \propto \text{tr} \delta(E - \hat{H}) \quad \text{"formally ok"}$$

but useful

typically: combinatorics how many ways  $\Omega$  can one distribute the energy  $E$  over quanta

## Microrcanonical ensemble summary

1.) Calculate Boltzmann entropy  $S = k_B \ln \Omega(E, V, N, \dots)$

number of states at given parameters and  $E \pm \delta$

Combinatorics  
or integration

$$\downarrow \Omega \rightarrow C(S) \Omega$$

then  $\ln \Omega \rightarrow \ln \Omega + \ln C$

a constant change of  $S$   
is irrelevant, since only  
 $\Delta S$  enters physical  
behavior

2.) Use  $dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN + \sum_{\alpha} \frac{F_{\alpha}}{T} d\alpha$

Therefore

$$\left( \frac{\partial S}{\partial E} \right)_V = \frac{1}{T}, \quad \left( \frac{\partial S}{\partial V} \right)_E = \frac{p}{T}$$

in general  $\frac{F_{\alpha}}{T} = \left( \frac{\partial S}{\partial \alpha} \right)_{rest, E}$

chemical potential

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{rest, E}$$

if  $\Omega(E)$  is "relatively" smooth  
in range  $E \pm \delta$

$\rightarrow$  large enough systems