Advanced Statistical Mechanics (2024)

Lecture 1

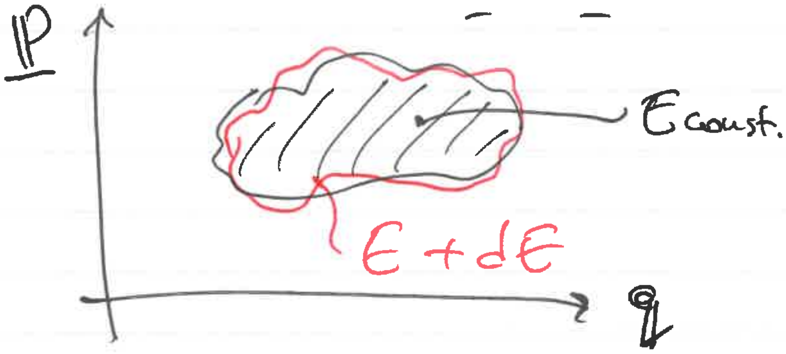
Brief recap of "Statistical physics"

- Microcanonical Ensemble

"phase space" $(\underline{\mathbb{P}}, \underline{\mathbb{q}})$

Hamiltonian $H(\mathbb{P}, \mathbb{q})$

Mean $H = E$



Find area: $\int d\mathbb{P}\, d\mathbb{q}$

$$E < H(\mathbb{P},\mathbb{q}) < E+dE$$

$$= \int \left(\Theta[E+dE-H] - \Theta[E-H] \right) d\mathbb{P}\, d\mathbb{q}$$

step-functions $\Theta(x)$

$$= dE \int \frac{d}{dE}\Theta(E-H)\, d\mathbb{P}\, d\mathbb{q}$$

$$\frac{d}{dx}\Theta(x) = \delta(x)$$

Define: $\boxed{\Omega(E) = \int \delta(E-H)\, d\mathbb{P}\, d\mathbb{q}}$

$\Omega(E)$ is the number of states with $H(p,q) = E$ (fixed E)

Define $\boxed{S(E) = k_B \ln \Omega(E)}$

the entropy of this microstate (with constant E)

Define probability $\rho(E)$:

Mean $\langle X(p,q) \rangle = \cancel{\int X(p,q)\rho(E)}$

$$= \frac{\int X(p,q)\, \delta(E - H(p,q))\, dp\, dq}{\Omega(E)}$$

Hence $\boxed{\rho(E) = \frac{\delta(E - H(p,q))}{\Omega(E)}}$ of a state within the microstate (E)

Normalised !

Easy to check:

$$\Omega(E) \equiv \int \Omega(E_1)\, \Omega(E - E_1)\, dE_1$$

Since $\Omega(E)$ is not normalised, there is an extra $\int \Omega(E)\, dE$

⊙ Canonical ensemble

of many microstates exchanging energy between

Define $e^{-\beta E}$ "weight"

Define probability — but first: its Normalisation factor

$$Z = \sum_{\text{all states}} e^{-\beta E} = \int dp\,dq\; e^{-\beta H(p,q)}$$

$\left(\int dp\,dq\right)$

re-order this summation: over microstates

$$Z = \sum_{\substack{\text{Microstates}\\(E)}} e^{-\beta E} \cdot \Omega(E)$$

$\Omega(E) \to e^{\ln \Omega}$

$$\boxed{Z = \sum_{\substack{\text{microstates}\\(E)}} e^{-\beta\left(E - kT \ln \Omega(E)\right)}}$$

Probability $\rho(E) = \frac{1}{Z} e^{-\beta\left(E - TS(E)\right)}$

Define: "free energy" of a microstate

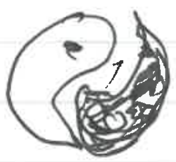
$$F(E) = E - TS(E)$$

This effect of multiplicity of states $\Omega(E)$, or $S(E)$, increases the probability $\rho(E)$

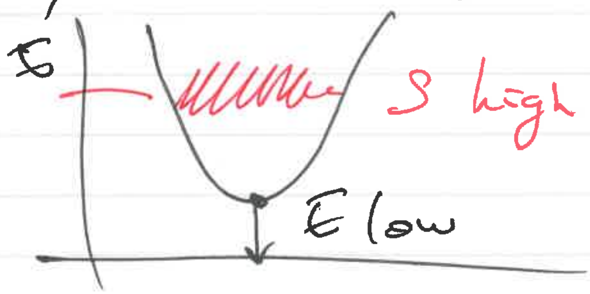
Maximum (mode) probability is when

(in a large system this is also the average and median)

$$\boxed{E - TS(E)} \text{ is minimal}$$



$\downarrow$	$\downarrow$
min E for equilibrium	max $S(E)$ for equilibrium



"T" is the switch between two trends

Finding equilibrium

How fast?

Barriers (metastability)?

Mechanism of this?