Statistical Mechanics

Aims to connect microscopic interactions to thermodynamic properties

Starting point: Boltzmann's Entropy formula,

$$S = k_B \ln \Omega (N, V, U)$$

Corresponding F.E. $S(N,V,U)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

or $\frac{dS}{k_B} = d\ln\Omega = \frac{1}{k_BT}dU + \frac{P}{k_BT}dV - \frac{\mu}{k_BT}dN$

Derivatives: $\left.\frac{\partial \ln\Omega}{\partial U}\right)_{V,N} = \frac{1}{k_BT}$ $\left.\frac{\partial \ln\Omega}{\partial N}\right)_{U,V} = -\frac{\mu}{k_BT}$

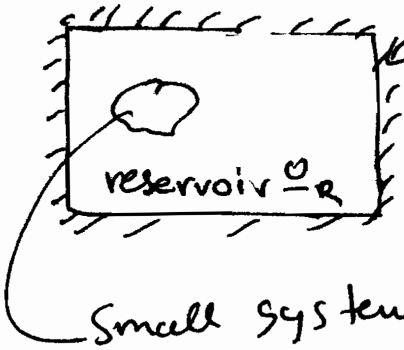
$\left.\frac{\partial \ln\Omega}{\partial V}\right)_{U,N} = \frac{P}{k_BT}$

Microstates with common properties (e.g. N, V, U) belong to a statistical mechanical "ensemble".

In the "microcanonical" ensemble (const. N, V, U) all microstates are equally probable, as per the fundamental postulate introduced in §3.6.

How about microstate probabilities in different ensembles - e.g. "canonical" N, V, T ensemble

→ Process akin to Legendre Transformation ←



total system, const. NVU

Ω states

Small system const. NVT microstate i, U_i

$$\Omega_R(U_R) = \Omega_R(U - U_i)$$

$$\rightarrow P_i \propto \Omega_R(U-U_i) = \exp\left[\ln\left[\Omega_R(U-U_i)\right]\right]$$

$$\ln \Omega_R(U-U_i) = \ln \Omega_R(U) - U_i \underbrace{\frac{\partial \ln \Omega_R}{\partial U}}_{1/k_BT} + \cdots$$

$$\therefore \quad \boxed{P_i \propto \exp\left(-\frac{U_i}{k_BT}\right)}$$

Probabilities of microstates no longer uniform. $\exp(-U_i/k_BT)$ is known as "Boltzmann factor"

In order to find the absolute probability of a microstate, need to normalize:

$$Q(N,V,T) = \sum_{\substack{\text{all} \\ \text{microstates } i}} \exp(-U_i/k_BT)$$

Average energy $\quad \langle U \rangle = \dfrac{1}{Q} \sum_i U_i \exp(-U_i/k_BT)$

But...
$$\frac{\partial \ln Q}{\partial(1/k_BT)} = \frac{1}{Q}\sum_i \frac{\partial}{\partial(1/k_BT)} e^{-U_i/k_BT} = -\frac{1}{Q}\sum_i U_i e^{-U_i/k_BT}$$

$$= -\langle U \rangle$$

For $S = k_B \ln \Omega$ $\qquad d\ln\Omega = \dfrac{1}{k_BT}dU + \dfrac{P}{k_BT}dV - \dfrac{\mu}{k_BT}dN$

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Take first transform of S/k_B :

$$\frac{S}{k_B} - \frac{U}{k_B T} = - \frac{U - TS}{k_B T} = - \frac{A}{k_B T} = f\left(\frac{1}{k_B T}, V, N\right)$$

$$\left.\frac{\partial(-A/k_B T)}{\partial(1/k_B T)}\right)_{V,N} = -U \quad \therefore \quad \boxed{-\frac{A}{k_B T} = \ln Q}$$

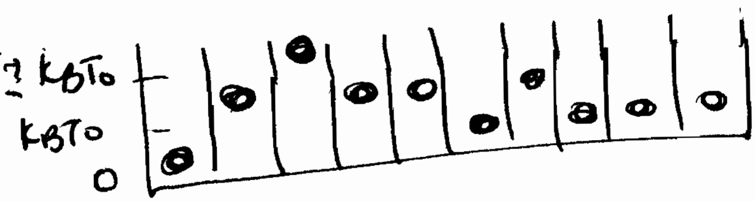
$$d \ln Q = -U \, d\left(\frac{1}{k_B T}\right) + \frac{P}{k_B T} dV - \frac{\mu}{k_B T} dN$$

Gibbs entropy formula:

$$\underbrace{-\sum_i P_i \ln P_i =}_{\text{NVT ensemble}} - \sum_i P_i \left[-\ln Q - \frac{U_i}{k_B T}\right] = \ln Q + \frac{U}{k_B T} =$$

$$= \frac{-A + U}{k_B T} = \frac{S}{k_B} \quad \underline{\text{QED}}$$

Example



10 spheres
3 levels

$T = T_0/3$

$\Omega(0) = 1 \quad \Omega(1) = 10 \quad \Omega(2) = 55 \quad \ldots$

$$Q = \sum_i e^{-U_i/k_B T} = 1 \cdot \exp(0) + 10 \cdot e^{-3} + \\ + 55\, e^{-6} + 220\, e^{-9} + \cdots$$

$$= 1 + 0.498 + 0.136 + 0.027 + \cdots$$

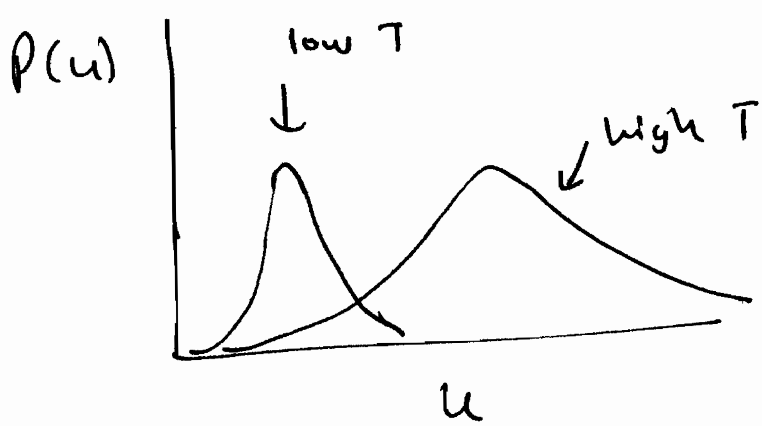
Probabilities of energy levels go down quickly for this – low – temperature

In general, the probability of a given energy U is

$$P(U) \propto \underbrace{\Omega(U)}_{\text{number of microstates}} \times \underbrace{e^{-U/k_BT}}_{\text{Boltzmann factor}} \quad \text{at const } N, V, T$$

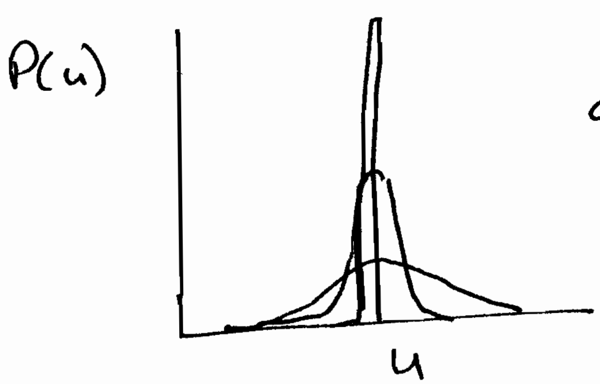
$\Omega(U)$ goes up quickly with U

e^{-U/k_BT} goes down " "



In classical thermodynamics, at given N, V, T only one energy can exist. However, this is not strictly true, esp. seen for small systems

given N, V, T



as system size goes ↑, $P(U)$ becomes more like a δ function