

microscopic \rightarrow macroscopic
 Statistical mechanics

essence of statistical mechanics
 large N limit
 deviations are negligible (improbable)

Ω multiplicity
 $g(\epsilon)$ density of states
 $S = k_B \ln g$ entropy
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 entropy will add

$$\frac{1}{T} = k_B \left(\frac{\partial S}{\partial U} \right)$$

two systems in contact exchange energy to maximize entropy

$$T_1 = T_2$$

"Laws":

- 0: $T_1 = T_2, T_2 = T_3 \rightarrow T_1 = T_3$
- 1: Heat is energy
- 2: S increases when you remove a constraint
- 3: $S \rightarrow$ finite value when $T \rightarrow 0$
 $S(T=0) = k_B \ln [g(T=0)]$

$$P(\epsilon) \sim e^{-\beta \epsilon}; \beta = \frac{1}{k_B T}$$

$$P(\epsilon) = \frac{e^{-\beta \epsilon}}{\sum_{\text{states}} e^{-\beta \epsilon}} \quad \left. \vphantom{\sum} \right\} Z \text{ partition function}$$

$$U = \langle E \rangle = \sum p(\epsilon) \epsilon$$

$$= \frac{\sum \epsilon e^{-\beta \epsilon}}{Z} = k_B T^2 \frac{\partial Z}{\partial T}$$

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

$$Z = \int_{\epsilon} g(\epsilon) e^{-\beta \epsilon} d\epsilon$$

$$dU = T dS - p dV + \underbrace{\mu}_{\text{chemical potential}} dN$$

$\underbrace{\quad}_{\text{heat}} \quad \underbrace{\quad}_{\text{work}} \quad \underbrace{\quad}_{\text{particle numbers}}$

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

Free energy:

Const temp. (Bath)

$$F = U - TS$$

$$= -k_B T \ln Z \rightarrow Z = e^{-\beta F}$$

- const. T: Helmholtz $F = U - TS$
- const. P: Enthalpy $H = U + pV$
- const. T, P: Gibbs $G = U - TS + pV$

$$dF = d(U - TS)$$

$$= T dS - p dV - \mu dN - T dS - S dT$$

$$dF = -S dT - p dV + \mu dN$$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N}$$

$$\ln N! \approx N \ln N$$