IV Microcanonical ensemble

Closed and isolated system
⇒ number of particles/states fixed
energy fixed

IV.1 Microcanonical ensemble for discrete states

N states, energy E,
What are probabilities p_i in equilibrium?
Each state p_i has energy E_i ⇒ all p_i with $E_i \neq E$ vanish.
Isolated, closed system ⇒ entropy is maximised in equilibrium

⇒ p_i with $E_i = E$ have to be chosen such that
$-\sum_{i=1}^{N} p_i \ln p_i$ is maximised

$N(E)$: number of states with energy E
denote states with energy E by $i=1,\dots,N(E)$

maximise $-\sum_{i=1}^{N(E)} p_i \ln p_i$ $\qquad F(\{p_i\}) = -\sum_{i=1}^{N(E)} p_i \ln p_i$

constraint $\sum_{i=1}^{N(E)} p_i = 1$ $\qquad G(\{p_i\}) = \sum_{i=1}^{N(E)} p_i$

Lagrange multiplier

$$0 = \frac{d}{dp_i}\left(F + \lambda G\right) = \left[-\ln p_i - 1 + \lambda\right]$$

⇒ all p_i are identical

$$\sum_{i=1}^{N(E)} p_i = 1 \quad \Rightarrow \quad p_i = \frac{1}{N(E)}$$

$$p_i = \begin{cases} \frac{1}{N(E)} & E_i = E \\ 0 & E_i \neq E \end{cases}$$

"microcanonical ensemble"

$\boxed{\text{All states with the same energy are equally probable}}$

$$S = -k_B \sum_{i=1}^{N} p_i \ln p_i = -k_B \sum_{i=1}^{N(E)} p_i \ln p_i$$

$$= -k_B \sum_{i=1}^{N(E)} \frac{1}{N(E)} \ln \frac{1}{N(E)} = k_B \ln N(E)$$

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

$\boxed{\text{Entropy is the logarithm of the number of accessible states}}$

<u>Example:</u> Einstein solid

3D lattice with N lattice sites

three harmonic oscillators at each site

frequency ω identical for all oscillators

$$H = \hbar\omega \sum_{i=1}^{3N} n_i + \frac{3}{2}N\hbar\omega$$

↑ number of energy quanta in i-th oscillator

Find $S(E, N)$:

Given N and $E = \hbar\omega M + \frac{3}{2} N \hbar\omega$

M ← number of quanta

$N(E) = ?$

$$N(E) = \frac{(3N+M-1)!}{M!\,(3N-1)!}$$

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3N distinguishable oscillators

M indistinguishable quanta

$$S = k_B \ln N(E) = k_B \ln \frac{(3N+M-1)!}{M!\,(3N-1)!}$$

M, N large → Stirling's formula $N \ln(N) - N$

$$S \approx k_B (3N+M) \ln(3N+M) - k_B M \ln M - k_B 3N \ln(3N)$$

→ complete knowledge of the system

Example: Find heat capacity C_N

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N \quad \rightarrow \text{ need } \; U(T,N)$$

$\rightarrow$ need T

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial M}\right)_N = \frac{k_B}{\hbar\omega}\left[\ln(3N+M) - \ln M\right]$$

$$= \frac{k_B}{\hbar\omega} \ln\left(1 + \frac{3N}{M}\right)$$

$$\Rightarrow \quad 1 + \frac{3N}{M} = e^{\beta\hbar\omega} \qquad\qquad \beta = \frac{1}{k_B T}$$

$$\Rightarrow \quad M = \frac{3N}{e^{\beta\hbar\omega} - 1}$$

$$\Rightarrow \quad E = \frac{3N\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{3}{2} N\hbar\omega$$

$$C_N = \left(\frac{\partial E}{\partial T}\right)_N = \left(\frac{\partial \beta}{\partial T}\right)_N \left(\frac{\partial E}{\partial \beta}\right)_N$$

$$= + \frac{1}{k_B T^2} 3N\hbar\omega \frac{\hbar\omega\, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = \frac{3N(\hbar\omega)^2}{k_B T^2} \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$