IV.2 Microcanonical ensemble for N-particle system

N particles, energy E, volume V
Find density $\varrho(\vec{x}^N)$ in thermodynamic equilibrium

Energy of phase space point $\vec{x}^N$: $H(\vec{x}^N)$

energy continuous → have to allow finite energy range
$[E, E+\Delta E]$ ← very small

$$\varrho(\vec{x}^N) = 0 \quad \text{if} \quad H(\vec{x}^N) < E \text{ or } H(\vec{x}^N) \geq E + \Delta E$$

Constraint $\displaystyle\int_{E \leq H(\vec{x}^N) \leq E+\Delta E} d\vec{x}^N \, \varrho(\vec{x}^N) = 1$

Isolated, closed system ⇒ Entropy is maximized

$$\text{Maximize} \quad -\int_{E \leq H(\vec{x}^N) \leq E+\Delta E} d\vec{x}^N \, \varrho(\vec{x}^N) \ln C_N \varrho(\vec{x}^N) = F[\varrho]$$

$$G[\varrho] \equiv \int_{E \leq H(\vec{x}^N) \leq E+\Delta E} d\vec{x}^N \, \varrho(\vec{x}^N) - 1$$

$$0 = \frac{d}{d\varrho(\vec{x}^N)} (F + \lambda G) = \begin{cases} -\ln C_N \varrho(\vec{x}^N) - 1 + \lambda & \text{for } H(\vec{x}^N) \in [E, E+\Delta E] \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \quad C_N \varrho(\vec{x}^N) = e^{\lambda - 1} \quad \text{for } H(\vec{x}^N) \in [E, E+\Delta E]$$

⇒ $\varrho(\vec{x}^N)$ is constant on "energy shell" $[E, E+\Delta E]$

Normalization:

$$\boxed{\rho(\vec{x}^N) = \begin{cases} \dfrac{1}{\Omega_{\Delta E}(E,V,N)} & H(\vec{x}^N) \in [E, E+\Delta E] \\ 0 & \text{otherwise} \end{cases}}$$

where $\Omega_{\Delta E}(E,V,N) = \int\limits_{E \le H(\vec{x}^N) \le E+\Delta E} d\vec{x}^N$ = "volume of energy shell"

as $\Delta E \to 0$ rewrite

"surface area of energy surface"

$$\Omega_{\Delta E}(E,V,N) \approx \Delta E \frac{d\Omega(E,V,N)}{dE} \equiv \Delta E \, \Sigma(E,V,N)$$

with $\Omega(E,V,N) = \int\limits_{H(\vec{x}^N) \le E} d\vec{x}^N$ = "phase space volume with energy less than E"

What is the entropy?

$$S = -k_B \int d\vec{x}^N \rho(\vec{x}^N) \ln \rho(\vec{x}^N) C_N$$

$$= -k_B \int\limits_{E \le H(\vec{x}^N) \le E+\Delta E} d\vec{x}^N \frac{1}{\Omega_{\Delta E}(E,V,N)} \ln \frac{C_N}{\Omega_{\Delta E}(E,V,N)}$$

$$= k_B \ln \frac{\Omega_{\Delta E}(E,V,N)}{C_N} \int\limits_{E \le H(\vec{x}^N) \le E+\Delta E} d\vec{x}^N \frac{1}{\Omega_{\Delta E}(E,V,N)}$$

$$= k_B \ln \frac{\Omega_{\Delta E}(E,V,N)}{C_N}$$

Compare with discrete system:

$\rightarrow \quad \dfrac{\Omega_{\Delta E}(E,V,N)}{C_N} \equiv N(E)$ "number of states with energy E"

$\Rightarrow C_N$ = "phase space volume of one state"

Simplification of entropy for large N:

$$\Omega(E,V,N) = \int_0^E \Sigma(E',V,N)\,dE' \underset{\text{energy surfaces increase}}{\leq} \int_0^E \Sigma(E,V,N)\,dE'$$

$$= E\,\Sigma(E,V,N)$$

$$= \frac{E}{\Delta E}\,\Omega_{\Delta E}(E,V,N)$$

$$\Rightarrow \Omega_{\Delta E}(E,V,N) \leq \Omega(E,V,N) \leq \frac{E}{\Delta E}\,\Omega_{\Delta E}(E,V,N)$$

$$\Rightarrow \underbrace{\ln \Omega_{\Delta E}(E,V,N)}_{\sim N} \leq \underbrace{\ln \Omega(E,V,N)}_{\sim N} \leq \underbrace{\ln \Omega_{\Delta E}(E,V,N)}_{\sim N} + \underbrace{\ln\left(\frac{E}{\Delta E}\right)}_{\sim \ln N}$$

$$\frac{E}{\Delta E} \lesssim N$$

$\Rightarrow$ as N becomes large $\ln \Omega_{\Delta E}(E,V,N) \simeq \ln \Omega(E,V,N)$

$$\Rightarrow \boxed{S = k_B \ln \frac{\Omega(E,V,N)}{C_N}} \quad \text{for large } N$$

IV.3 Summary

concepts: microcanonical ensemble
phase space volume

facts: all states with the same energy are equally probable
$S = k_B \ln N(E)$ / $S = k_B \ln \dfrac{\Omega(E,V,N)}{C_N}$

tools: Lagrange multipliers
combinatorics
Stirling's formula
functional derivatives
combinatorics $\rightarrow N(E,V,N) \rightarrow S(E,V,N) \rightarrow T(E,V,N) \rightarrow$ thermodynamics

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