$$\Rightarrow \mu = \frac{1}{k_B T} \equiv \beta$$

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Result:

$$\boxed{n_i = \frac{e^{-\beta E_i}}{\sum_{i=1}^{N} e^{-\beta E_i}}}$$

distribution of the canonical ensemble

features
- all states have a positive probability
- all states with the same energy have the same probability
- the probability of a state decays exponentially with its energy

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Abbreviation:

$$Z(T) = \sum_{i=1}^{N} e^{-\frac{1}{k_B T} E_i}$$

"partition function" of the system

How do we get to thermodynamics?

$$S = k_B \frac{1}{k_B T} U + k_B \ln Z(T)$$

$$\Rightarrow \quad U - TS = -k_B T \ln Z(T)$$

$$\Rightarrow \quad F = -k_B T \ln Z(T)$$ Helmholtz free energy

Recipe:

microscopic model $\rightarrow Z(T) = \sum_{i=1}^{N} e^{-\frac{1}{k_B T} E_i}$

$\rightarrow F = -k_B T \ln Z(T) \rightarrow$ thermodynamics

V.1.2 Example (discrete system)

Einstein solid:

3D lattice with N lattice sites
three harmonic oscillators at each site
frequency ω identical for all oscillators

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

n_j: number of quanta in oscillator j

state i: $(n_1, n_2, \ldots, n_{3N})$

partition function

$$Z = \sum_{\{(n_1,\ldots,n_{3N})\}} e^{-\beta\hbar\omega\sum_{j=1}^{3N} n_j - \frac{3}{2}\beta N\hbar\omega}$$

$$= \sum_{\{(n_1,\ldots,n_{3N})\}} e^{-\beta\hbar\omega n_1} e^{-\beta\hbar\omega n_2} \cdots e^{-\beta\hbar\omega n_{3N}} e^{-\frac{3}{2}\beta N\hbar\omega}$$

$$= \left(\sum_{n_1=0}^{\infty} e^{-\beta\hbar\omega n_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta\hbar\omega n_2}\right) \cdots \left(\sum_{n_{3N}=0}^{\infty} e^{-\beta\hbar\omega n_{3N}}\right) e^{-\frac{3}{2}\beta N\hbar\omega}$$

$$= \left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^{3N}\left(e^{-\frac{1}{2}\beta\hbar\omega}\right)^{3N} = \left(e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}\right)^{-3N}$$

$$\Rightarrow F = -k_B T \ln Z = 3Nk_B T \ln\left(e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}\right)$$

internal energy:

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_N = 3N \frac{e^{\frac{1}{2}\beta\hbar\omega} + e^{-\frac{1}{2}\beta\hbar\omega}}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}} \frac{1}{2}\hbar\omega$$

$$\frac{3N(\hbar\omega)^2}{k_B T^2 \left(e^{\frac{1}{2}\hbar\omega\beta} - e^{-\frac{1}{2}\hbar\omega\beta}\right)^2}$$

heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_N = \left(\frac{\partial U}{\partial \beta}\right)_N \left(\frac{\partial \beta}{\partial T}\right)_N = -\frac{3}{2}N\hbar\omega \, \frac{\frac{1}{2}\hbar\omega}{k_B T^2} \, \frac{\left(e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}\right)^2 - \left(e^{\frac{1}{2}\beta\hbar\omega} + e^{-\frac{1}{2}\beta\hbar\omega}\right)^2}{\left(e^{\frac{1}{2}\hbar\omega\beta} - e^{-\frac{1}{2}\beta\hbar\omega}\right)^2}$$

V.1.3 General framework (continuous system)

Setup:

N particles, classical mechanics

$\vec{q}_i$: generalized position of particle i
$\vec{p}_i$: generalized momentum of particle i $\quad i=1,\dots,N$

phase space points

$$\vec{x}^N = (\vec{q}_1,\dots,\vec{q}_N,\vec{p}_1,\dots,\vec{p}_N)$$

system described by probability density

$\rho(\vec{x}^N)$: $\quad \rho(\vec{x}^N)\,d\vec{x}^N$ = probability to find system in phase space volume $[\vec{x}^N, \vec{x}^N + d\vec{x}^N]$

Energy of phase space point:

$H(\vec{x}^N)$ (Hamiltonian)

Entropy of a probability density

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

$$C_N = \begin{cases} \frac{1}{h^{3N}} & \text{distinguishable particles} \\ \frac{1}{h^{3N} N!} & \text{indistinguishable particles} \end{cases}$$

"phase space volume of a single state"

average energy $\quad U = \int d\vec{x}^N \, H(\vec{x}^N)\, \rho(\vec{x}^N)$

Closed system in contact with heat bath at temperature T $\Rightarrow$ average energy fixed

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<u>Program</u>: Maximize

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

under the constraints

$$\int d\vec{x}^N \rho(\vec{x}^N) = 1$$

and $$\int d\vec{x}^N H(\vec{x}^N) \rho(\vec{x}^N) = U$$

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<u>Method</u>: Lagrange multipliers λ and μ

$$0 = \frac{\partial}{\partial \rho(\vec{x}^N)} \Big[-\int d\vec{x}^N \rho(\vec{x}^N) \ln[C_N \rho(\vec{x}^N)] + \lambda \Big(\int d\vec{x}^N \rho(\vec{x}^N) - 1 \Big) + \mu \Big(U - \int d\vec{x}^N H(\vec{x}^N) \rho(\vec{x}^N) \Big) \Big]$$

$$= -\ln[C_N \rho(\vec{x}^N)] - 1 + \lambda - \mu H(\vec{x}^N)$$

$$\Rightarrow \rho(\vec{x}^N) = \frac{1}{C_N} e^{\lambda - 1} e^{-\mu H(\vec{x}^N)}$$

Normalization $\Rightarrow$ $$\rho(\vec{x}^N) = \frac{e^{-\mu H(\vec{x}^N)}}{\int d\vec{x}^N e^{-\mu H(\vec{x}^N)}}$$

Still have to find μ:

$\mu = \mu(U)$: $$U = \frac{\int d\vec{x}^N H(\vec{x}) e^{-\mu H(\vec{x}^N)}}{\int d\vec{x}^N e^{-\mu H(\vec{x}^N)}}$$