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

Ⓣ 11/15

Program: Maximize

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

under the constraints

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

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

↓ 11/13

Method: Lagrange multipliers λ and μ

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

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

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

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

Still have to find μ:

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

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

$$= -k_B \int d\vec{x}^N \frac{e^{-\mu H(\vec{x}^N)}}{\int d\vec{y}^N e^{-\mu H(\vec{y}^N)}} \left[\ln C_N + \mu H(\vec{x}^N) - \ln \int d\vec{y}^N e^{-\mu H(\vec{y}^N)}\right]$$

$$= -k_B \ln C_N + k_B \mu U + k_B \ln \int d\vec{y}^N e^{-\mu H(\vec{y}^N)}$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = k_B \mu + k_B U \frac{\partial \mu}{\partial U} - k_B \underbrace{\frac{\int d\vec{y}^N e^{-\mu H(\vec{y}^N)} H(\vec{y}^N)}{\int d\vec{y}^N e^{-\mu H(\vec{y}^N)}}}_{U} \frac{\partial \mu}{\partial U}$$

$$= k_B \mu$$

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

Result:

$$\boxed{\rho(\vec{x}^N) = \frac{e^{-\beta H(\vec{x}^N)}}{\int d\vec{y}^N e^{-\beta H(\vec{y}^N)}}}$$

Abbreviation:

$$\boxed{Z(T) = \int d\vec{x}^N \frac{e^{-\beta H(\vec{x}^N)}}{C_N}}$$

partition function (dimensionless)

$$S = -k_B \ln C_N + k_B \frac{1}{k_B T} U + k_B \ln \int d\vec{x}^N e^{-\mu H(\vec{x}^N)}$$

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

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

→ same procedure as for discrete system

Useful property:

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right) = -k_B T \ln Z(T) - T\left(-k_B \ln Z(T) - k_B T \frac{\partial \ln Z(T)}{\partial T}\right)$$

$$= k_B T^2 \left(\frac{\partial \ln Z(T)}{\partial T}\right) = -\left(\frac{\partial \ln Z(T)}{\partial \beta}\right)$$

V.1.4 Example (continuous system — ideal gas)

N particles, positions $\vec{r}_i$, momenta $\vec{p}_i$

$$H(\vec{x}^N) = \begin{cases} \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2} & \text{all } \vec{r}_i \text{ within volume } V \\ \infty & \text{otherwise} \end{cases}$$

$$Z(T) = \int d\vec{x}^N \, \frac{e^{-\beta H(\vec{x}^N)}}{C_N}$$

$$= \frac{1}{h^{3N} N!} \int d\vec{r}_1 \cdots \int d\vec{r}_N \int d\vec{p}_1 \cdots \int d\vec{p}_N \, e^{-\beta H(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)}$$

$$= \frac{1}{h^{3N} N!} V^N \int d\vec{p}_1 \cdots \int d\vec{p}_N \, e^{-\frac{\beta}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2}}$$

$$= \frac{V^N}{h^{3N} N!} \left(\int d\vec{p} \, e^{-\frac{\beta}{2m}\vec{p}^{\,2}} \right)^N = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$\Rightarrow \quad F = -k_B T \ln Z(T) = -k_B T \ln \left[\frac{V^N}{h^{3N} N!} (2\pi m k_B T)^{\frac{3N}{2}} \right]$$

$$= -N k_B T \ln \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + k_B T \ln N!$$

$$\approx -N k_B T - N k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \qquad \lambda \equiv \sqrt{\frac{h^2}{2\pi m k T}}$$

Stirling $\quad = -N k_B T - N k_B T \ln \left(\frac{V}{N\lambda^3} \right)$

"thermal wavelength"
quantum mechanical wavelength of a particle with energy $k_B T$

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

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V,N} = N k_B + N k_B \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} N k_B$$

$$U = F + TS = \frac{3}{2} N k_B T$$

microscopic derivation of velocity distribution:

$$\varrho(\vec{x}^N) = \frac{\frac{1}{C_N}\, e^{-\beta H(\vec{x}^N)}}{Z(T)} = \frac{\cancel{h^{3N} N!}\; e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}}}{\cancel{h^{3N} N!}\; V^N (2\pi m k_B T)^{3N/2}} \quad \text{if all } \vec{r}_i \text{ within } V$$

probability density to find a particle with velocity $\vec{v}$:

$$P_{\vec{V}}(\vec{v}) = \int d\vec{x}^N \varrho(\vec{x}^N)\; \delta\left(\frac{\vec{p}_1}{m} - \vec{v}\right)$$

$$P_{\vec{V}}(\vec{v}) = \frac{1}{V^N (2\pi m k_B T)^{3N/2}} \int d\vec{x}^N\; e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}}\, \delta\left(\frac{\vec{p}_1}{m} - \vec{v}\right)$$

$$= \frac{1}{(2\pi m k_B T)^{3N/2}} \int d\vec{p}_1 \ldots \int d\vec{p}_N\; e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}}\, \delta\left(\frac{\vec{p}_1}{m} - \vec{v}\right)$$

$$= \frac{1}{(2\pi m k_B T)^{3/2}} \int d\vec{p}_1\, e^{-\frac{\beta}{2m}\vec{p}_1^{\,2}}\, \delta\left(\frac{\vec{p}_1}{m} - \vec{v}\right)$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left\{-\frac{m\vec{v}^{\,2}}{2 k_B T}\right\}$$

→ Maxwell distribution

V.1.5 Example (mixed system)

Ideal gas of N identical atoms in box of volume V.
each atom has spin $\frac{1}{2}$ and magnetic moment μ.
external magnetic field $\vec{H}$

State of the system: $(\vec{x}^N, s_1, \ldots, s_N)$ $s_i = \pm 1$

Energy : $E(\vec{x}, s_1, \ldots, s_N) = \frac{1}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} - \frac{1}{2}\mu H \sum_{i=1}^{N} s_i$

partition function:

$$Z(T) = \frac{1}{c_N}\int d\vec{x}^N \sum_{\{(s_1,\ldots,s_N)\}} e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} + \frac{\beta\mu H}{2}\sum_{i=1}^{N} s_i}$$

$$= \frac{V^N}{N! h^{3N}}\int d\vec{p}_1 \ldots \int d\vec{p}_N \sum_{s_1\in\{-1,1\}} \ldots \sum_{s_N\in\{-1,1\}} e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} + \frac{\beta\mu H}{2}\sum_{i=1}^{N} s_i}$$

$$= \frac{V^N}{N! h^{3N}}\left(\int d\vec{p}\, e^{-\frac{\beta}{2m}\vec{p}^{\,2}}\right)^N \left(e^{-\frac{\beta\mu H}{2}} + e^{\frac{\beta\mu H}{2}}\right)^N$$

$$= \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}\left(2\cosh\left(\frac{\beta\mu H}{2}\right)\right)^N$$

11/15

$$\ln Z(T) = N\left\{1 + \ln\left[\frac{2V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right] + \ln\cosh\frac{\beta\mu H}{2}\right\}$$

internal energy:

$$U = -\frac{\partial \ln Z}{\partial \beta} = +\frac{3}{2}N\frac{1}{\beta} - N\frac{\sinh\frac{\beta\mu H}{2}}{\cosh\frac{\beta\mu H}{2}}\frac{\mu H}{2}$$

$$= \frac{3}{2}N k_B T - \frac{N\mu H}{2}\tanh\frac{\beta\mu H}{2}$$