

## § 4.3 例 1: 古典理想气体

$$H(\mathbf{q}, \mathbf{p}) = \sum_i \frac{1}{2m_i} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2)$$

$$\begin{aligned} Z &= \frac{1}{N!} \frac{1}{h^{3N}} \int \dots \int d\mathbf{q}_1 \dots d\mathbf{q}_N d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta H} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} V^N \left( \int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}} dp \right)^{3N} \\ &= \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \left( \sqrt{\frac{2m}{\beta}} \pi \right)^{3N} \\ &= \frac{1}{N!} \left( \frac{V (2\pi m k_B T)^{\frac{3}{2}}}{h^3} \right)^N \end{aligned}$$

$$\begin{aligned} \star \int_{-\infty}^{\infty} e^{-ax^2} dx &= \frac{1}{\sqrt{a}} \int_{-\infty}^{\infty} e^{-y^2} dy \\ &= \frac{1}{\sqrt{a}} \sqrt{\pi} = \sqrt{\frac{\pi}{a}} \end{aligned}$$

★ 一般に相互作用のない系では

$$\begin{aligned} Z &= \sum_r e^{-\beta E_r} \\ &= \sum_r e^{-\beta (e_1 + e_2 + \dots + e_N) / r} \\ &= \left( \sum_r e^{-\beta e_i r} \right)^N \end{aligned}$$

Z 的求法 热力学函数

$$A = -k_B T \ln Z$$

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

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

$$S = - \left( \frac{\partial A}{\partial T} \right)_{V, N} = -k_B N \left( \ln N - 1 - \ln \frac{V(2\pi m k_B T)^{3/2}}{h^3} - \frac{3}{2} \right)$$

$$= +k_B N \left( \frac{5}{2} - \ln N + \ln \frac{V(2\pi m k_B T)^{3/2}}{h^3} \right)$$

↓

$$\underline{\underline{\pi, p = \bar{T} p = T'' (2.42)}}$$

$$p = - \left( \frac{\partial A}{\partial V} \right)_{T, N} = k_B T \cdot N \cdot \frac{1}{V} = \frac{N k_B T}{V}$$

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状态方程式

$$\mu = \left( \frac{\partial A}{\partial N} \right)_{T, V} = k_B T \left( 1 + \ln N - 1 - \ln \frac{V(2\pi m k_B T)^{3/2}}{h^3} \right)$$

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

$$E = A + T p$$

$$= \frac{3}{2} N k_B T$$