正则系综的几率分布

$$\rho_s = \frac{1}{Z_N} e^{-\beta E_s}, \ (\beta = \frac{1}{kT})$$

系统处于能量为E_s的量子态s的几率

配分函数 $Z_N = \sum_s e^{-\beta E_s} = Z_N(\beta, \{y_\lambda\})$

内能

$$\bar{E} = \sum_s E_s \rho_s = \frac{1}{Z_N} \sum_s E_s e^{-\beta E_s}$$

$$= \frac{1}{Z_N}\left(-\frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}\right) = -\frac{\partial}{\partial \beta} \ln Z_N$$

外界作用力

$$\bar{Y}_\lambda = \sum_s \frac{\partial E_s}{\partial y_\lambda} \rho_s = \frac{1}{Z_N} \sum_s \frac{\partial E_s}{\partial y_\lambda} e^{-\beta E_s}$$

$$= \frac{1}{Z_N}\left(-\frac{1}{\beta} \frac{\partial}{\partial y_\lambda} \sum_s e^{-\beta E_s}\right) = -\frac{1}{\beta} \frac{\partial}{\partial y_\lambda} \ln Z_N$$

特例：$y_\lambda = V$, $\bar{Y}_\lambda = -p \Rightarrow p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N$

熵

$$S \xlongequal[\text{得到}]{\text{不难}} k\left(\ln Z_N - \beta \frac{\partial}{\partial \beta} \ln Z\right)$$

自由能

$$F = \bar{E} - TS = -kT \ln Z_N$$

能量涨落

$$\overline{(E-\bar{E})^2} = \overline{(E^2 - 2E\cdot\bar{E} + \bar{E}^2)}$$

$$= \overline{E^2} - 2\bar{E}^2 + \bar{E}^2 = \overline{E^2} - \bar{E}^2$$

$$\overline{E^2} = \sum_s E_s^2 \rho_s = \frac{1}{Z_N} \sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z_N} \frac{\partial^2}{\partial \beta^2} \sum_s e^{-\beta E_s} = \frac{1}{Z_N} \frac{\partial^2}{\partial \beta^2} Z_N$$

$$= \frac{1}{Z_N} \frac{\partial}{\partial \beta}\left(Z_N \frac{\partial}{\partial \beta} \ln Z_N\right) = \bar{E}^2 - \frac{\partial \bar{E}}{\partial \beta}$$

$$\overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \left(\frac{\partial \bar{E}}{\partial T}\right)_{V,N} = kT^2 C_V$$

$$\frac{\sqrt{\overline{(E-\bar{E})^2}}}{\bar{E}} = \frac{\sqrt{kT^2 C_V}}{\bar{E}} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

经典极限

条件 $\begin{cases} \lambda_T \ll \bar{\delta_r} \\ \Delta E \ll kT \end{cases}$

假设只有一种粒子，总数为N，总自由度 $s = Nr$，r为粒子自由度

$$\rho(q_1, \cdots, q_s; p_1, \cdots, p_s)\, d\Omega = \frac{1}{Z_N N! h^s} e^{-\beta H(q_1, \cdots, p_s)} d\Omega$$

$$d\Omega = dq_1 \cdots dq_s\, dp_1 \cdots dp_s$$

$$Z_N = \frac{1}{N! h^s} \int \cdots \int e^{-\beta H(q_1, \cdots, p_s)} dq_1 \cdots dp_s.$$

全同粒子不可分辨

考虑满足经典极限条件的单原子分子理想气体并忽略分子的内部自由度。

$$Z_N = \frac{1}{N! h^{3N}} \int e^{-\beta H} d\Omega$$

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^{N} \varepsilon_i$$

$$d\Omega = \prod_{i=1}^{N} d\omega_i$$

$$d\omega_i = dx_i\, dy_i\, dz_i\, dp_{x_i}\, dp_{y_i}\, dp_{z_i}$$

$$Z_N = \frac{1}{N! h^{3N}} \int \cdots \int e^{-\beta \sum_i \varepsilon_i} \prod_i d\omega_i$$

$$= \frac{1}{N! h^{3N}} \int \cdots \int \prod_{i=1}^{N} \{e^{-\beta \varepsilon_i} d\omega_i\}$$

$$= \frac{1}{N!} \prod_{i=1}^{N} \left\{\frac{1}{h^3} \int e^{-\beta \varepsilon_i} d\omega_i\right\}$$

又 $Z = \frac{1}{h^3} \int e^{-\beta \varepsilon_i} d\omega_i$

$$= \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}$$

$Z_N = \frac{Z^N}{N!} \Rightarrow \ln Z_N = N \ln Z - \ln N!$

系综配分函数与子系配分函数的关系

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z_N = -N \frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} NkT$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N = \frac{N}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{NkT}{V}$$

$$S = Nk\left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z\right) - k \ln N!$$

$$= \frac{3}{2} Nk \ln T + Nk \ln \frac{V}{N} + \frac{3}{2} Nk \left\{\frac{5}{3} + \ln\left[\frac{2\pi m k}{h^2}\right]\right\}$$