玻尔兹曼分布 → 麦克斯韦速度分布

→ 速率分布 $n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}v^2} v^2 dv$

$a_l = \omega_l e^{-\alpha-\beta\varepsilon_l}$

$= \left(\frac{V}{h^3} dp_x dp_y dp_z\right) e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}$

在 $dv_x dv_y dv_z$ 范围内的分子数为

$N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z$

又 $\frac{V}{h^3}\iiint e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)} dp_x dp_y dp_z = N$

$\Rightarrow e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}$

单位体积内在 $dv_x dv_y dv_z$ 范围内的分子数为

$f(v_x, v_y, v_z) dv_x dv_y dv_z$

$= n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z$

能量均分定理 对于处在温度为T的平衡状态的经典系统，粒子能量中每一个独立的平方项的平均值等于 $\frac{1}{2}kT$

$\varepsilon = \varepsilon_p + \varepsilon_q$ 动能+势能

$\varepsilon_p = \frac{1}{2}\sum_{i=1}^{r} a_i p_i^2$

$\overline{\frac{1}{2}a_1 p_1^2} = \frac{1}{N}\int \frac{1}{2}a_1 p_1^2 e^{-\alpha-\beta\varepsilon} \frac{dq_1\cdots dq_r dp_1\cdots dp_r}{h_0^r}$

$= \frac{1}{Z_1}\int \frac{1}{2}a_1 p_1^2 e^{-\beta\varepsilon} \frac{dq_1\cdots dq_r dp_1\cdots dp_r}{h_0^r}$

$\int_{-\infty}^{+\infty} \frac{1}{2}a_1 p_1^2 e^{-\frac{\beta}{2}a_1 p_1^2} dp_1 = \underbrace{\left(-\frac{p_1}{2\beta} e^{-\frac{\beta}{2}a_1 p_1^2} dp_1\right)\Big|_{-\infty}^{+\infty}}_{=0} + \frac{1}{2\beta}\int_{-\infty}^{+\infty} e^{-\frac{\beta}{2}a_1 p_1^2} dp_1$

$\prod_{i=1}^{r}$

$\overline{\frac{1}{2}a_1 p_1^2} = \frac{1}{2\beta}\frac{1}{Z_1}\underbrace{\int e^{-\beta\varepsilon}\frac{dq_1\cdots dq_r dp_1\cdots dp_r}{h_0^r}}_{Z_1} = \frac{1}{2}kT$

同理可证 $\overline{\frac{1}{2}b_1 q_1^2} = \frac{1}{2}kT$

单原子分子

$\varepsilon = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)$

$U = \frac{3}{2}NkT$

双原子分子

$\varepsilon = \frac{1}{2m}(p_x^2+p_y^2+p_z^2) + \frac{1}{2I}\left(p_\theta^2 + \frac{1}{\sin^2\theta}p_\varphi^2\right) + \frac{1}{2m_\mu}p_r^2 + u(r)$

为什么 $U = \frac{5}{2}NkT$ ？

↓ 引入量子统计理论

$\varepsilon = \varepsilon^t + \varepsilon^v + \varepsilon^r$

$Z_1 = \sum_l \omega_l e^{-\beta\varepsilon}$

$= Z_1^t Z_1^v Z_1^r$

$U = -N\frac{\partial}{\partial\beta}\ln Z_1$

$= U^t + U^v + U^r$

t: $Z_1^t = V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}$

$U = \frac{3}{2}NkT$

v: $\varepsilon_n = (n+\frac{1}{2})\hbar\omega$ 量子化！

$Z_1^v = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$

$U^v = \frac{N\hbar\omega}{2} + Nk\theta_v e^{-\frac{\theta_v}{T}}$

其中 $k\theta_v = \hbar\omega \to \theta_v \sim 10^3 K$

可忽略

r: $\varepsilon^r = \frac{l(l+1)\hbar^2}{2I}$ 量子化！

$Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\frac{\beta\hbar^2}{2I}l(l+1)}$

其中 $k\theta_r = \frac{\hbar^2}{2I} \to \frac{\theta_r}{T} \ll 1$

$Z_1^r = \frac{2I}{\beta\hbar^2}$

$U^r = NkT$

对单原子理想气体 非定域系

$S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right)$

经典理论给出 $Z_1 = V\left(\frac{2\pi m}{h_0^2\beta}\right)^{\frac{3}{2}}$

得 $S = \frac{3}{2}Nk\ln T + Nk\ln V + \frac{3}{2}Nk\left[1+\ln\left(\frac{2\pi mk}{h_0^2}\right)\right]$

① 依赖于 h_0 ② 不符合广延量要求

量子理论

① 经典极限 $S = k\ln\frac{\Omega_{M.B.}}{N!}$ (减 $k\ln N!$)

② h_0 取为 h 注意是 h 不是 $\hbar$

以及 $\ln N! = N(\ln N - 1)$

得 $S = \frac{3}{2}Nk\ln T + Nk\ln\frac{V}{N} + \frac{3}{2}Nk\left[\frac{5}{3} + \ln\left(\frac{2\pi mk}{h^2}\right)\right]$

$F = -NkT\ln Z_1 + kT\ln N!$

$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

$= -kT\ln\frac{Z_1}{N}$

$= kT\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right]$

经典极限条件下

$e^{\alpha} = \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \gg 1$

$\mu < 0$