Focus 7

经典理论的失败

- 维恩位移定律：$\lambda_{max}T = b = 2.898\times10^{-3}\ m\cdot K$
- 斯特藩-玻尔兹曼定律：$E(T) = c''T^4$，$c'' = \frac{8\pi^5k^4}{15h^3c^3}$
- 瑞利-金斯定律：$P(\lambda,T) = \frac{8\pi kT}{\lambda^4}$

普朗克分布公式 $P(\lambda,T) = \frac{8\pi hc}{\lambda^5[\exp(\frac{hc}{\lambda kT})-1]}$ $\Theta_E = \frac{h\nu}{k}$ 爱因斯坦温度

光电效应：$h\nu = E_k + \phi$ 德布罗意关系：$\lambda = \frac{h}{p}$

爱因斯坦公式：$C_{V,m} = 3R\left(\frac{\Theta_E}{T}\right)^2\left(\frac{\exp(\frac{\Theta_E}{2T})}{\exp(\frac{\Theta_E}{T})-1}\right)^2$

一维薛定谔方程：$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$

归一化：$\int_{-\infty}^{\infty}|\psi|^2dx = 1$

本征值形式：$\hat{H}\psi = E\psi$, a.w. $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

算符 $\hat{x} = x\times$；$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$；$\hat{E}_k = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$；$\hat{H} = \hat{T}+\hat{V} = \frac{\hat{p}_x^2}{2m}+\hat{V}$

Hermitian Operators：$\hat\Omega$；本征值方程：$\hat\Omega\psi = \omega\psi$

$\int\psi_i^*\hat\Omega\psi_j\,d\tau = \left(\int\psi_j^*\hat\Omega\psi_i\,d\tau\right)^*$，$\hat\Omega_1+\hat\Omega_2$ and $\hat\Omega_1\hat\Omega_2$ also hermitian

Orthogonality：$\int\psi_i^*\psi_j\,d\tau = 0\ (i\neq j)$

当系统处于叠加态 $\psi = \sum_k c_k\psi_k$ 时，$P(W_k)\propto|c_k|^2$

平面波函数：e^{ikx}；e^{-ikx}，均为本征函数

$p=+k\hbar$　$p=-k\hbar$　对应概率分别为 $|A|^2$ and $|B|^2$

余弦函数的叠加性质：$\psi(x) = \cos kx = (e^{ikx}+e^{-ikx})/2$

任意波函数展开：$\psi = \sum_k c_k\psi_k$

$1 = \int_{-\infty}^{\infty}\psi^*\psi\,d\tau = \sum_k|c_k|^2$．$\langle\Omega\rangle = \int\psi^*\hat\Omega\psi\,d\tau$

若 ψ 为 $\hat\Omega$ 的本征函数，$\langle\Omega\rangle = w$

若 ψ 为叠加态，则 $\langle\Omega\rangle = \sum_k|c_k|^2W_k$

海森堡不确定性原因：$\Delta p_q\Delta q \geq \frac{\hbar}{2}$；$[A^2,B] = A[A,B]+[A,B]A$

对易子 $[\hat\Omega_1,\hat\Omega_2] = \hat\Omega_1\hat\Omega_2 - \hat\Omega_2\hat\Omega_1$；基本对易关系 $[\hat x,\hat p] = -[\hat p,\hat x] = i\hbar$

$[\hat H,\hat p_x]$ $\begin{cases} =0, & \text{when } V=V_0\text{，可同时精确测量} \\ \neq0, & \text{when } V=\frac12kx^2\text{，不可} \end{cases}$

概率密度 $|\psi|^2$；合格波函数条件：单值、连续、有限、一阶导连续

波函数一般解 $\psi = Ae^{ikx}+Be^{-ikx}$，代表动量分别为 $+k\hbar$ 与 $-k\hbar$ 的平面波叠加

能量 $E_k = \frac{k^2\hbar^2}{2m}\geq0$

受限粒子（一维势箱）的量子化现象（1D）

$\psi(0)=\psi(L)=0$；$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$　$n=1,2,3,\cdots$

$E_n = \frac{n^2h^2}{8mL^2}$ & $\langle p_x^2\rangle = \frac{n^2h^2}{4L^2}$　$\langle x^2\rangle = L^2\left(\frac13-\frac{1}{2n^2\pi^2}\right)$

when $n=1$：$\langle x\rangle = \frac{L}{2}$；$\langle x^2\rangle = L^2\left(\frac13-\frac{1}{2\pi^2}\right)$

二维势箱（2D）

$\hat H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)$；箱内 $V=0$，箱外 $V=\infty$

$\psi_{n_1,n_2}(x,y) = \frac{2}{\sqrt{L_1L_2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi x}{L_2}$

能量本征值：$E_{n_1n_2} = \left[\left(\frac{n_1}{L_1}\right)^2+\left(\frac{n_2}{L_2}\right)^2\right]\frac{h^2}{8m}$

三维势箱（3D）

$\psi_{n_1,n_2,n_3}(x,y,z) = \sqrt{\frac{8}{L_1L_2L_3}}\prod_i\sin\frac{n_i\pi x_i}{L_i}$，$E=\frac32kT$

Degeneracy：When $L_1=L_2=L$，(n_1,n_2) 与 (n_2,n_1) 能量相同

Tunnelling Effect:

$\begin{cases} x<0, & \psi = Ae^{ikx}+Be^{-ikx}\ \text{（振荡）} \\ 0\leq x\leq W, & \psi = Ce^{kx}+De^{-kx}\ \text{（指数衰减）} \\ x>W, & \psi = A'e^{ikx}\ \text{（振荡）} \end{cases}$　a.w. $\begin{cases} k = \frac{\sqrt{2mE}}{\hbar} \\ K = \frac{\sqrt{2m(V_0-E)}}{\hbar} \end{cases}$

连续性条件：$\psi, \frac{d\psi}{dx}$ 在边界均连续　透射比正比于概率比

透射系数 $T = \left(1+\frac{(e^{kW}-e^{-kW})^2}{16\varepsilon(1-\varepsilon)}\right)^{-1}$ → 透射概率，$\varepsilon = \frac{E}{V_0}$　势垒高度 V_0　势垒宽度 W

when $kW\gg1$，$T\approx16\varepsilon(1-\varepsilon)e^{-2kW}$

Harmonic Oscillator

势能 $V(x)=\frac12k_fx^2$，k_f：力常数　有效质量 $\mu = \frac{m_Am_B}{m_A+m_B}$，$w=\sqrt{k_f/\mu}$，$w_2 = w_1\sqrt{\frac{\mu_1}{\mu_2}}$，$\tilde\nu = \frac{\nu}{c}$

$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac12k_fx^2\psi = E\psi$ (*)

令 $\xi = x\sqrt{\frac{mw}{\hbar}}$，$\varepsilon = \frac{2E}{\hbar w}$，则 (*) $\Longleftrightarrow \frac{d^2\psi}{d\xi^2} = (\xi^2-\varepsilon)\psi$

渐近行为 $\xi\to+\infty$，解得 $H(\xi)e^{\pm\frac{\xi^2}{2}}$，only $e^{-\frac{\xi^2}{2}}$ is acceptable

波函数通解 $\psi_v(x) = N_vH_v(y)e^{-\frac{y^2}{2}}$，a.w. $y=\frac{x}{\alpha}$，$\alpha = \left(\frac{\hbar^2}{mk_f}\right)^{\frac14}$

能量量子化 $E_v = \frac{\hbar w}{2}(2v+1)$，$v=0,1,2,\cdots$

最低能量 $E_0 = \frac12\hbar w\neq0$，$E_{v+1}-E_v = \hbar w$

$H_0(y)=0$；$H_1(y)=2y$；$H_2(y)=4y^2-2$；$H_3(y)=8y^3-12y$；

$H_4(y)=16y^4-48y^2+12$；$H_5(y)=32y^5-160y^3+120y$；

$H_6(y)=64y^6-480y^4+720y^2-120$.

Rotational Motion

$\vec J = \vec r\times\vec p$ 角动量 $=(yp_z-zp_y,\ zp_x-xp_z,\ xp_y-yp_x)$

对于二维，$l_z = xp_y-yp_x$，$E = \frac{l_z^2}{2I}$

量子转动薛定谔方程：$x=r\cos\phi$，$y=r\sin\phi$

$\begin{cases} -\frac{\hbar^2}{2I}\frac{d^2\psi}{d\phi^2} = E\psi \\ \psi(\phi) = e^{im_l\phi} \\ E = \frac{\hbar^2m_l^2}{2I} \end{cases}$　周期性边界条件 $\psi(\phi)=\psi(\phi+2\pi)$

$e^{im_l2\pi}=1 \Rightarrow m_l=0,\pm1,\pm2,\cdots$

归一化 $\psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}$

双原子分子：频率 $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$，$k=1857\ N/m$

角动量算符 $\hat l_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$；$\hat l_z\psi = m_l\hbar\psi$；$l_z = m_l\hbar$

$[\hat\phi,\hat l_z] = i\hbar\neq0$，则 l_z 已知时，角位置不定

Rotation in 3D

拉普拉斯算符：$\nabla^2 = \frac1r\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2}\Lambda^2$

a.w. $\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$

刚性转子的转动薛定谔方程：$-\frac{\hbar^2}{2I}\Lambda^2Y_{l,m_l}(\theta,\phi) = EY_{l,m_l}(\theta,\phi)$

球谐函数 $Y_{l,m_l}(\theta,\phi)$

$\begin{cases} l=0,1,2,\cdots \\ m_l=0,\pm1,\pm2,\cdots \end{cases}$ & $E = l(l+1)\frac{\hbar^2}{2I}$，$I=\mu R^2$

总角动量 $J=\sqrt{l(l+1)}\hbar$；z分量 $l_z = m_l\hbar$

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{\frac12}$
1	0	$\left(\frac{3}{4\pi}\right)^{\frac12}\cos\theta$
1	±1	$\mp\left(\frac{3}{8\pi}\right)^{\frac12}\sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{\frac12}(3\cos^2\theta-1)$
2	±1	$\mp\left(\frac{15}{8\pi}\right)^{\frac12}\cos\theta\sin\theta e^{\pm i\phi}$
2	±2	$\left(\frac{15}{32\pi}\right)^{\frac12}\sin^2\theta e^{\pm2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{\frac12}(5\cos^3\theta-3\cos\theta)$

角度依赖性 $Y_{l,m_l}(\theta,\phi) = e^{im_l\phi}f(\theta)$

角动量算符 $\begin{cases} \hat l_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right) \\ \hat l_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right) \\ \hat l_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right) \end{cases}$ 互不对易

$[\hat l^2,\hat l_z]=0$　球面薛定谔：$-\frac{\hbar^2}{2I}\nabla^2\psi = E\psi$　$\nabla^2Y_{l,m} = -l(l+1)Y_{l,m}$

简并度：E_l 对应 $2l+1$ 个不同的量子态.

高斯积分公式：$\int_{-\infty}^{\infty}e^{-au^2}du = \sqrt{\frac{\pi}{a}}$

$\langle p_x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\hat p_x\psi(x)\,dx$，期望值

$\psi(x) = \frac{1}{N}\sum_{k=1}^{N}\cos k\pi x$，$x\in[-1,1]$

$\Delta x = \sqrt{\langle x^2\rangle-\langle x\rangle^2}$；$\Delta p_x = \sqrt{\langle p_x^2\rangle-\langle p_x\rangle^2}$

$\langle[\hat x,\hat p_x]\rangle = \langle\hat x\hat p_x\rangle-\langle\hat p_x\hat x\rangle$

Hermite 多项式递推：$yH_v = \frac12H_{v+1}+vH_{v-1}$

本征值：eigenvalue

[Evaluate the commutator $[\hat{H},\hat{x}]$ for $\hat{V}=0$ and $\hat{V}=\frac{1}{2}kx^2$]

(i) $[\hat{H},\hat{x}]\psi = [\frac{\hat{p}_x^2}{2m},\hat{x}]\psi + [\hat{V},\hat{x}]\psi$

$= \frac{\hat{p}_x^2}{2m}\hat{x}\psi - \hat{x}\frac{\hat{p}_x^2}{2m}\psi = -\frac{\hbar^2}{2m}\frac{d^2(x\psi)}{dx^2} - x(-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2})$

$= -\frac{\hbar^2}{2m}(x\frac{d^2\psi}{dx^2} + 2\frac{d\psi}{dx} - x\frac{d^2\psi}{dx^2}) = -\frac{\hbar^2}{m}\frac{d}{dx}\psi$

$[\hat{H},\hat{x}] = -\frac{\hbar^2}{m}\frac{d}{dx}$. so do (ii)

[$V_0 = 2eV$, $E = 1.5eV$, $W = 100pm$, 求贯穿概率]

$K = \sqrt{\frac{2m(V_0-E)}{\hbar}} = 1.55\times10^{11} m^{-1}$, $\varepsilon = \frac{E}{V_0} = 0.75$,

$KW = 1.55\times10^{11}\times100\times10^{-12} = 15.5$

$T = \left[1+\frac{(e^{KW}-e^{-KW})^2}{16\varepsilon(1-\varepsilon)}\right]^{-1} = 1.03\times10^{-13}$

[At what displacements is the probability desity a maximum for a state of a harmonic oscillator with $v=3$]

$\psi_v(x) = N_v H_v(y) e^{-\frac{y^2}{2}}$, $y=\frac{x}{\alpha}$; $f(y) = |\psi_v(x)|^2$

$H_3(y) = 8y^3 - 12y$

令 $f'(y) = 0 = -8N_3^2 H_3(y) e^{-y^2}(2y^4 - 9y^2 + 3) = 0$

解得 $y = \pm\sqrt{\frac{9\pm\sqrt{57}}{4}}$ when $H_3(y)=0$

$x = \cdots\alpha$. At the nodes $f(y)=0 \Rightarrow y=0$舍

[By considering the integral $\int_0^{2\pi}\psi_{m_l}^*\psi_{m_l'}d\phi$, $m_l\neq m_l'$, confirm that wavefunctions for a particle in a ~~ring~~ ring with different values of the quantum ~~nu~~ number m_l are mutually orthogonal]

$I = \int_0^{2\pi}\psi_{m_l}^*\psi_{m_l'}d\phi = \int_0^{2\pi}\frac{1}{\sqrt{2\pi}}e^{-im_l\phi}\cdot\frac{1}{\sqrt{2\pi}}e^{im_l'\phi}d\phi$

$= \frac{1}{2\pi}\int_0^{2\pi}e^{i(m_l'-m_l)\phi}d\phi = \left[\frac{1}{i\Delta m}e^{i\Delta m\phi}\right]_0^{2\pi} = 0$

among which, $e^{i\Delta m 2\pi} = 1$

The wavefunction of a particle in a ring is

$\psi_{m_l} = e^{im_l\phi}$

[Demonstrate that the Planck distribution reduces to the Rayleigh - Jeans Law at wavelength]

When x is small, $e^x = 1-x$

the $\rho_p(\lambda,T) = \frac{8\pi hc}{\lambda^5}\cdot\frac{1}{x} = \frac{8\pi kT}{\lambda^4}$

[Calculate the energy density in the range $1000 cm^{-1}$ to $1010 cm^{-1}$ inside a cavity at a) 25°C. b) 4K]

$\rho(\tilde{\nu},T) = 8\pi hc\tilde{\nu}^3\frac{1}{e^{hc\tilde{\nu}/kT}-1}$

$\Delta U = \rho(\tilde{\nu}_{avg},T)\cdot\Delta\tilde{\nu}$

[$S = 343 W/m^2$, 吸收率 $a = 70\%$, 辐射通量 $\sigma = 5.672\times10^{-8}(T/K)^4 W\cdot m^{-2}$]

$aS = \sigma T^4$, $\lambda_{max}T = b \Rightarrow \lambda_{max} = 11.4\mu m$

[25-26 秋季考试] Q1

Consider a quantum mechanical particle of mass m constrained to move on a ring of radius r in the ~~xy~~ xy plane. Its position is defined by the angular coordinate $\phi\in[0,2\pi)$. Evaluate whether each of the following wavefunctions is a physically valid state for this particle. State "Acceptable" or "Unacceptable" and provide a brief justification. For those that are acceptable, determine the appropriate normalization constant.

(1) $\cos\frac{5}{2}\phi$

(2) $\sin(\phi+0.3\pi)$

(3) $\sin\phi + 2\cos\phi$

Focus 13 Statistical Thermodynamics

The first law: $\Delta U = Q + W$

Entropy: $S = k\ln W$

Boltzmann Distribution: $N_i \propto \exp(-\beta\varepsilon_i)$, a.w. $\beta = \frac{1}{k_B T}$

归一化: $\frac{N_i}{N} = \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}$, a.w. q: Molecular partition function

$f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(\frac{-mv^2}{2k_B T}\right) v^2$

Weight of a configuration: $W = \frac{N!}{N_0!N_1!N_2!\cdots}$ 权重Ω

Stirling's approximation: $\begin{cases} \ln x! = x\ln x - x \\ x! \simeq \sqrt{2\pi}\, x^{x+\frac{1}{2}} e^{-x} \end{cases}$

$\frac{N_i}{N} = \frac{\exp(-\beta\varepsilon_i)}{q} = \frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{q}$

一个简单的二能级系统: $\varepsilon_0 = 0$, $\varepsilon_1 = \varepsilon$, $\varepsilon = hc\tilde{\nu}$

有 $\begin{cases} q = 1 + e^{-\beta\varepsilon} \\ \frac{N_1}{N} = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \end{cases}$

一个能级ε_k有g_k个量子状态,即简并度为g_k

能级布局公式: $\frac{N_k}{N} = \frac{g_k \exp(-\beta\varepsilon_i)}{q}$, a.w. $q = \sum_k g_k e^{-\beta\varepsilon_k}$

$q = \sum_{v=0}^{\infty} e^{-\beta v\varepsilon} = \frac{1}{1-e^{-\beta\varepsilon}}$

能级布局概率: $P_v = \frac{e^{-\beta v\varepsilon}}{q}$

由 $\varepsilon_i = \varepsilon_i^T + \varepsilon_i^R + \varepsilon_i^V + \varepsilon_i^E$, $q = q^T \cdot q^R \cdot q^V \cdot q^E$

[平动配分函数]

对于质量m粒子在长度为X的一维盒子中运动,其能级为

$$\varepsilon_n = \frac{h^2 n^2}{8mX^2}, \quad n = 1, 2, 3, \ldots$$

一维配分函数 $q_x^T = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} X$

热波长(粒子的热德布罗意波长) $\Lambda = \frac{h}{(2\pi mkT)^{\frac{1}{2}}}$, then $q_x^T = \frac{X}{\Lambda}$

三维: $q^T = q_x^T q_y^T q_z^T = \frac{V}{\Lambda^3}$

[转动配分函数]

$E_J = hc\tilde{B}J(J+1)$, 简并度 $g_J = 2J+1$

$q^R = \sum_{J=0}^{\infty} (2J+1)\exp(-\beta hc\tilde{B}J(J+1))$

a.w. 转动常数(cm^{-1}) $\tilde{B} = \frac{h}{8\pi^2 cI}$ 波数, $I = \mu R^2$ = 约化质量(x键长)^2

当高温($kT \gg hc\tilde{B}$), $q^R = \frac{kT}{hc\tilde{B}} = \frac{T}{\sigma\Theta_R}$

a.w. 转动特征温度 $\Theta_R = \frac{hc\tilde{B}}{k}$, 对称数$\sigma$ $\begin{cases} \text{同核双原子:2} \\ \text{异核:1} \end{cases}$

[振动配分函数]

$\varepsilon_v = \hbar\omega v$, $q^V = \frac{1}{1-e^{-\beta\hbar\omega}} = \frac{1}{1-e^{-\Theta_V/T}}$, a.w. $\Theta_V = \frac{\hbar\omega}{k}$ 振动特征温度

[电子配分函数] $q^E = g_{E,0}$

$\langle\varepsilon\rangle = -\frac{1}{q}\left(\frac{\partial q}{\partial\beta}\right)_V$

若以基态能量ε_{gs}为参考零点, $\langle\varepsilon\rangle = \varepsilon_{gs} - \frac{1}{q}\left(\frac{\partial q}{\partial\beta}\right)_V$

谐振子的基态能量为 $\varepsilon_{gs} = \frac{1}{2}\hbar\omega = \frac{1}{2}hc\tilde{\nu}$, a.w. $\tilde{\nu}$ 波数$=\frac{1}{\lambda}$

平动: $\langle\varepsilon^T\rangle = \frac{3}{2}kT$; 转动: $\langle\varepsilon^R\rangle = kT$

振动: $\langle\varepsilon^V\rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}$, 高温近似 $\simeq kT$

For example: H_2O

3N: 9; 平动: 3 → $\frac{3}{2}kT$; 转动: 3 → $\frac{3}{2}kT$; 振动 3N-6 = 3个模式, 3kT

总: $\frac{3}{2}kT + \frac{3}{2}kT + 3kT = 6kT$

正则分布

系统处于能量E_i的概率 $P_i = \frac{N_i}{N} = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} = \frac{\exp(-\beta E_i)}{Q}$

a.w. Q: 正则配分函数

可区分粒子系统(如晶体) $Q = q^N$

不可区分粒子系统(如气体) $Q = \frac{q^N}{N!}$

$\langle E\rangle = \sum_i P_i E_i = -\frac{1}{Q}\left(\frac{\partial Q}{\partial\beta}\right)_V$

系统内能 $U(T) = U(0) + N\langle\varepsilon\rangle = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial\beta}\right)_V$

$C_V = -\frac{\partial}{\partial T}\left(\frac{N\partial\ln q}{\partial\beta}\right)_V$

可区分: $S = \frac{U(T)-U(0)}{T} + Nk\ln q$

不可分: $S = \frac{U(T)-U(0)}{T} + Nk\ln q - k\ln N! \simeq \frac{U(T)-U(0)}{T} + Nk\ln\frac{q}{N} + Nk$

with 正则配分函数: $S = \frac{U(T)-U(0)}{T} + k\ln Q$

[二能级系统]

$$\begin{cases} q = 1 + e^{-\beta\varepsilon} \\ \langle\varepsilon\rangle = \frac{\varepsilon}{q} \\ S = \frac{N\varepsilon k\beta}{1+e^{\beta\varepsilon}} + Nk\ln(1+e^{-\beta\varepsilon}) \end{cases}$$

亥姆霍兹自由能 $\begin{cases} A(T) = U(T) - TS \\ A(T) - A(0) = -kT\ln Q \end{cases}$

吉布斯自由能

$G(T,P,N) = A(T,V,N) + PV$

$= G(0) - kT\ln Q + kTV\left(\frac{\partial\ln Q}{\partial V}\right)_T$

For perfect gas: $= G(0) - kTN\ln\frac{q}{N}$

经典配分函数

$Q = \frac{1}{h^{3N}}\iint e^{-\beta E} dr^N dp^N$

For perfect gas: $Q = \frac{V^N}{\Lambda^{3N} N!}$

萨克尔-特鲁德方程: $S_m = R\ln\frac{V_m e^{\frac{5}{2}}}{N_A\Lambda^3} = R\ln\frac{V_m e^{\frac{5}{2}}}{N_A\Lambda^3}$

For example $f_1 = \frac{4e^{-\varepsilon/kT}}{2+4e^{-\varepsilon/kT}}$, $\varepsilon = 450\,\text{cm}^{-1}$, $k = 0.695\,\text{cm}^{-1}/\text{K}$

数密度 $n(h) = n(0)e^{-mgh/kT}$

由 $p = nkT$, $p(h) = p(0)e^{-mgh/kT}$

定义标高 $H = kT/mg$, $p(h) = p_0 e^{-h/H}$, $H = \frac{kT}{mg} = \frac{RT}{Mg}$

单个分子的平均能量

$\langle\varepsilon\rangle = \frac{\sum_i \varepsilon_i e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}$

Focus 14

Electric dipole moment: $1D \simeq 0.2e\cdot\text{Å} = 3.33564\times10^{-30}\ C\cdot m$

Polar vs. Nonpolar molecule: $\mu_{res}^2 = \mu_1^2+\mu_2^2+2\mu_1\mu_2\cos\theta$

$\vec{\mu} = \sum_J Q_J \vec{r}_J = \Sigma$ 电荷 $\times$ 位置矢量

Polarizability: $\mu^* = \alpha E$, $\alpha: C\cdot m^2/V$, among which $\alpha = \alpha' \cdot 4\pi\varepsilon_0$

$E = \frac{\mu^*}{\alpha' \cdot 4\pi\varepsilon_0}$

Charge-charge interaction: $V = \frac{Q_1Q_2}{4\pi\varepsilon_0 r}$ a.w. l:偶极长度

Charge-dipole interaction: $V = -\frac{Q_1 l Q_2}{4\pi\varepsilon_0 r^2} = -\frac{\mu_1 Q_2}{4\pi\varepsilon_0 r^2}$

Dipole-dipole interaction:

$V = \frac{1}{4\pi\varepsilon_0 r^3}\left\{\vec{\mu}_1\cdot\vec{\mu}_2 - \frac{3(\vec{\mu}_1\cdot\vec{r})(\vec{\mu}_2\cdot\vec{r})}{r^3}\right\}$, $V \propto -\frac{1}{r^6}$

Lennard-Jones 相互作用: $V = 4\varepsilon\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right\}$

a.w. ε:势阱深度, r_0:平衡距离

液体的总势能: $V = \sum_{ij} 4\varepsilon\left\{\left(\frac{r_0}{r_{ij}}\right)^{12} - \left(\frac{r_0}{r_{ij}}\right)^6\right\} - \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$

Surface tension: γ

Laplace equation: 对于半径 r 球形气泡, $F = 8\pi r\gamma$

$P_{in} - P_{out} = \Delta P = \frac{2\gamma}{r}$ 毛细作用 Capillary action

Surfactants 越大, 则 γ 越小; 反之则反之.

毛细上升公式 $\gamma = \frac{1}{2}\rho g r h$

向右步数 N_R, 向左步数 N_L, 定义净位移 $n = N_R - N_L$

特定构象 $\{N_R, N_L\}$ 的概率为 $P = \frac{W}{2^N} = \frac{N!}{\left(\frac{N+n}{2}\right)!\left(\frac{N-n}{2}\right)!\,2^N}$

由斯特林近似 $P = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}}\exp\left(-\frac{n^2}{2N}\right)$

构象熵 $S = k\ln W$ = Boltzmann costant $\times$ ln 微观状态数

The concept of self-assembly

$\langle n\rangle = \sum_{n=-N}^{N} n\,p(n) \simeq \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \times \frac{1}{2}\int_{-N}^{N} n\cdot\exp\left(-\frac{n^2}{2N}\right)dn = 0$

$\langle n^2\rangle = \sum_{n=-N}^{N} n^2 p(n) = N$

$\sqrt{\langle l^2 n^2\rangle} = l\sqrt{\langle n^2\rangle} = l\sqrt{N}$.