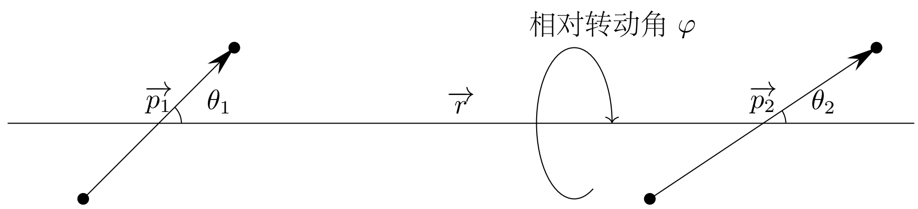
van der Waals 相互作用

(1) 由偶极矩在外场中的电势能公式

$$U = -\overrightarrow{p} \cdot \overrightarrow{E} \tag{1}$$

以及电偶极子的电场力公式

$$\overrightarrow{E} = \frac{1}{4\pi\varepsilon_0} \frac{3(\overrightarrow{p} \cdot \hat{r})\hat{r} - \overrightarrow{p}}{r^3} \tag{2}$$



可得其电势能大小为

$$\begin{aligned}
U(\theta_1, \theta_2, \varphi, r) &= -\overrightarrow{p} \cdot \overrightarrow{E} \\
&= -\frac{1}{4\pi\varepsilon_0} \frac{3(\overrightarrow{p_1} \cdot \hat{r})\hat{r} - \overrightarrow{p_1}}{r^3} \cdot \overrightarrow{p_2} \\
&= -\frac{1}{4\pi\varepsilon_0} \frac{3(\overrightarrow{p_1} \cdot \hat{r})\hat{r} \cdot \overrightarrow{p_2} - \overrightarrow{p_1} \cdot \overrightarrow{p_2}}{r^3} \\
&= -\frac{1}{4\pi\varepsilon_0} \frac{3p_1p_2\cos\theta_1\cos\theta_2 - p_1p_2(\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\varphi)}{r^3} \\
&= -\frac{1}{4\pi\varepsilon_0} \frac{2p_1p_2\cos\theta_1\cos\theta_2 - p_1p_2\sin\theta_1\sin\theta_2\cos\varphi}{r^3}
\end{aligned} \tag{3}$$

(2) 按照定义

$$\overline{U} = \frac{\displaystyle\int_1\int_2 U(\theta_1, \theta_2, \varphi, r)\exp\left(-\frac{U(\theta_1, \theta_2, \varphi, r)}{k_BT}\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2}{\displaystyle\int_1\int_2 \exp\left(-\frac{U(\theta_1, \theta_2, \varphi, r)}{k_BT}\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2} \tag{4}$$

令

$$\begin{aligned}
\beta =& \frac{1}{4\pi\varepsilon_0}\frac{p_1p_2}{r^3}\frac{1}{k_BT} \\
f(\Omega) =& 2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi
\end{aligned} \tag{5}$$

上式化为

$$\begin{aligned}
\overline{U} &= \frac{\displaystyle\int_1\int_2 k_BT\beta f(\Omega)\exp\left(\beta f(\Omega)\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2}{\displaystyle\int_1\int_2 \exp\left(\beta f(\Omega)\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2} \\
&= k_BT\beta\frac{\displaystyle-\frac{\partial}{\partial\beta}\int_1\int_2 \exp\left(\beta f(\Omega)\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2}{\displaystyle\int_1\int_2 \exp\left(\beta f(\Omega)\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2} \\
&= -k_BT\beta\frac{\partial}{\partial\beta}\ln\left(\int_1\int_2 \exp\left(\beta f(\Omega)\right)\mathrm{d}\Omega_1\mathrm{d}\Omega_2\right)
\end{aligned} \tag{6}$$

易知

$$\mathrm{d}\Omega_1 = \sin\theta_1 \mathrm{d}\theta_1 \mathrm{d}\varphi_1 \tag{7}$$

$$\mathrm{d}\Omega_2 = \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\varphi_2 \tag{8}$$

而由于引入了相对转动角，故

$$\mathrm{d}\Omega_1 \mathrm{d}\Omega_2 = \sin\theta_1 \mathrm{d}\theta_1 \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\varphi \tag{9}$$

下求积分

$$I = \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\varphi=0}^{2\pi} \exp(\beta f(\Omega)) \sin\theta_1 \mathrm{d}\theta_1 \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\varphi \tag{10}$$

代入题给近似

$$U(\theta_1, \theta_2, \varphi, r) \sim \frac{1}{4\pi\varepsilon_0} \frac{\overrightarrow{p_1} \cdot \overrightarrow{p_2}}{r^3} \ll k_B T \tag{11}$$

与 Tailor 展开公式

$$\exp(x) \approx 1 + x + \frac{1}{2}x^2 \qquad x \ll 1 \tag{12}$$

$$\begin{aligned} I \approx & \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\varphi=0}^{2\pi} \left(1 + \beta f(\Omega) + \frac{1}{2}\left(\beta f(\Omega)\right)^2\right) \sin\theta_1 \mathrm{d}\theta_1 \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\varphi \\ =& I_0 + I_1 + I_2 \end{aligned} \tag{13}$$

其中 I_0, I_1, I_2 分别对应其零阶，一阶，二阶近似的积分结果。易知

$$I_0 = 8\pi \tag{14}$$

$$I_1 = 0 \tag{15}$$

$$I_2 = \frac{8\pi}{3}\beta^2 \tag{16}$$

故有

$$\begin{aligned} \overline{U} &\approx -k_B T \beta \frac{\partial}{\partial \beta} \ln\left(8\pi(1 + \frac{\beta^2}{3})\right) \\ &= -k_B T \beta \frac{1}{1 + \frac{\beta^2}{3}} \cdot \frac{2\beta}{3} \\ &\approx -k_B T \frac{2\beta^2}{3} \\ &= -\frac{2}{3k_B T} \left(\frac{p_1 p_2}{4\pi\varepsilon_0}\right)^2 \cdot \frac{1}{r^6} \end{aligned} \tag{17}$$

(3) 在 p_2 处, 电场强度大小为

$$|\overrightarrow{E}| = \frac{p_1}{4\pi\varepsilon_0} \frac{\sqrt{1 + 3\cos^2\theta_1}}{r^3} \tag{18}$$

故其偶极矩大小为

$$|\overrightarrow{p}| = \alpha \frac{p_1}{4\pi\varepsilon_0} \frac{\sqrt{1 + 3\cos^2\theta_1}}{r^3} \tag{19}$$

代入 (1) 式

$$U = -\alpha \frac{p_1^2}{(4\pi\varepsilon_0)^2} \frac{1 + 3\cos^2\theta_1}{r^6} \tag{20}$$

(4) 此时，有

$$\overline{U}=\frac{\displaystyle\int_{\theta_1=0}^{\pi}U\exp\left(-\frac{U}{k_BT}\right)\sin\theta_1\mathrm{d}\theta_1}{\displaystyle\int_{\theta_1=0}^{\pi}\exp\left(-\frac{U}{k_BT}\right)\sin\theta_1\mathrm{d}\theta_1} \tag{21}$$

保留至零阶项

$$\overline{U}=-\alpha\frac{2p_1^2}{(4\pi\varepsilon_0)^2r^6} \tag{22}$$