高斯链的正则系综

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◦ 自由结合链的末端距 $\vec{R}$ 在正则系综平衡态下的概率密度：

$$\Phi(\vec{R}) \simeq \left(\frac{3}{2\pi n b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\|\vec{R}\|^2}{2nb^2}\right) \quad (n\to\infty \text{渐近})$$

△ 考虑键势能为 $u(\vec{r}) = \frac{3k_BT}{2b^2}\|\vec{r}\|^2$ 的链。一条 $n+1$ 个原子的链的势能

$$V(\{\vec{r}_i\}) = \sum_{i=1}^{n} \frac{3k_BT}{2b^2} \|\vec{r}_i\|^2 = \mathcal{H} \quad \text{overdamped ?}$$

△ 正则配分函数

$$Z = \int d\{\vec{r}_i\} \exp\left(-\frac{1}{k_BT}\sum_{i=1}^{n}\frac{3k_BT}{2b^2}\|\vec{r}_i\|^2\right)$$

$$= \int d\{\vec{r}_i\} \exp\left(-\sum_{i=1}^{n}\frac{3\|\vec{r}_i\|^2}{2b^2}\right)$$

$$= \left(\int d\vec{r} \exp\left(-\frac{3\|\vec{r}\|^2}{2b^2}\right)\right)^n$$

$$= \left(\frac{2\pi b^2}{3}\right)^{\frac{3n}{2}}$$

△ 高分子取构象 $\{\vec{r}_i\}$ 的概率密度（正则系综）

$$\Psi(\{\vec{r}_i\}) = Z^{-1} \exp\left(-\sum_{i=1}^{n}\frac{3\|\vec{r}_i\|^2}{2b^2}\right)$$

$$= \left(\frac{2\pi b^2}{3}\right)^{-\frac{3n}{2}} \exp\left(-\sum_{i=1}^{n}\frac{3\|\vec{r}_i\|^2}{2b^2}\right)$$

$$= \prod_{i=1}^{n}\left(\frac{2\pi b^2}{3}\right)^{-\frac{3}{2}} \exp\left(-\frac{3\|\vec{r}_i\|^2}{2b^2}\right)$$

$$= \prod_{i=1}^{n}\psi(\vec{r}_i), \quad \psi(\vec{r}) = \left(\frac{2\pi b^2}{3}\right)^{-\frac{3}{2}} \exp\left(-\frac{3\|\vec{r}\|^2}{2b^2}\right)$$

可见，我们所考虑的链，正则系综下的键概率 $\psi(\vec{r})$ 是高斯分布。故称该链是高斯链。

△ 高斯链的末端的概率密度（正则系综）

$$\Phi(\vec{R}) = \int_{\{\vec{r}_i\}} \delta\left(\vec{R} - \sum_{i=1}^{n}\vec{r}_i\right)\Psi(\{\vec{r}_i\})\, d\{\vec{r}_i\}$$

$$= \frac{1}{(2\pi)^3}\int d\vec{k}\, d\{\vec{r}_j\} \exp\left[i\vec{k}\cdot\left(\vec{R} - \sum_{j=1}^{n}\vec{r}_j\right)\right]\prod_{j=1}^{n}\left(\frac{2\pi b^2}{3}\right)^{-\frac{3}{2}} \exp\left(-\frac{3\|\vec{r}_j\|^2}{2b^2}\right)$$

$$= \frac{1}{(2\pi)^3}\left(\frac{3}{2\pi b^2}\right)^{\frac{3n}{2}}\int d\vec{k} \exp(i\vec{k}\cdot\vec{R})\int d\{\vec{r}_j\}\prod_{j=1}^{n}\exp\left(-i\vec{k}\cdot\vec{r}_j - \frac{3\|\vec{r}_j\|^2}{2b^2}\right)$$

$$= \frac{1}{(2\pi)^3}\left(\frac{3}{2\pi b^2}\right)^{\frac{3n}{2}}\int d\vec{k} \exp(i\vec{k}\cdot\vec{R})\left[\int d\vec{r} \exp\left(-i\vec{k}\cdot\vec{r} - \frac{3\|\vec{r}\|^2}{2b^2}\right)\right]^n$$

其中

$$\int d\vec{r} \exp\left(-i\vec{k}\cdot\vec{r} - \frac{3\|\vec{r}^2\|}{2b^2}\right) = \int dr_1 dr_2 dr_3 \exp\left(-i\sum_j k_j r_j - \frac{3\sum_j r_j^2}{2b^2}\right)$$

$$= \prod_{j=1}^{3}\int_{-\infty}^{\infty} dr_j \exp\left(-ik_j r_j - \frac{3r_j^2}{2b^2}\right)$$

$$= \prod_{j=1}^{3}\frac{2\pi b^2}{3} e^{-\frac{1}{6}b^2k_j^2}$$

$$= \left(\frac{2\pi b^2}{3}\right)^{3/2} e^{-\frac{1}{6}b^2k^2}$$

$$\therefore \Phi(\vec{R}) = \frac{1}{(2\pi)^3}\left(\frac{3}{2\pi b^2}\right)^{\frac{3n}{2}}\left(\frac{2\pi b^2}{3}\right)^{\frac{3n}{2}}\int d\vec{k} \exp(i\vec{k}\cdot\vec{R}) \exp\left(-\frac{1}{6}nb^2k^2\right)$$

$$= \frac{1}{(2\pi)^3}\prod_{j=1}^{3}\int \exp\left(ik_jR_j - \frac{1}{6}nb^2k_j^2\right) dk_j$$

$$= \frac{1}{(2\pi)^3}\prod_{j=1}^{3}\int \exp\left(ik_jR_j - \frac{1}{6}nb^2k_j^2\right)dk_j$$

$$= \frac{1}{(2\pi)^3}\left(\frac{6\pi}{nb^2}\right)^{\frac{3}{2}}\exp\left(-\frac{3\|\vec{R}\|^2}{2nb^2}\right)$$

$$= \left(\frac{3}{2\pi nb^2}\right)^{\frac{3}{2}}\exp\left(\frac{-3\|\vec{R}\|^2}{2nb^2}\right)$$

可见任意有限n个链节的高斯链的末端距概率分布是高斯分布（无需 $kb \ll 1$ 近似）。

$$\langle \vec{R}^2 \rangle = \int \vec{R}^2\,\Phi(\vec{R})\,d\vec{R}$$

$$= \left(\frac{3}{2\pi nb^2}\right)^{\frac{3}{2}}\int d\vec{R}\,\vec{R}^2\exp\left(-\frac{3\|\vec{R}\|^2}{2nb^2}\right)$$

$$= \left(\frac{3}{2\pi nb^2}\right)^{\frac{3}{2}}4\pi\int_0^\infty \rho^4\exp\left(-\frac{3\rho^2}{2nb^2}\right)d\rho$$

$$= \left(\frac{3}{2\pi nb^2}\right)^{\frac{3}{2}}4\pi\,\frac{1}{3}\sqrt{\frac{\pi}{6}}\,(nb^2)^{\frac{5}{2}}$$

$$= nb^2$$