自由结合链的末端距概率密度

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△ 球面上的均匀分布：三维欧几里德空间$\mathbb{R}^3$的位置向量$\vec{r}$满足概率密度$\psi(\vec{r})$，

$$\psi(\vec{r})=\frac{1}{4\pi b^2}\delta(\|\vec{r}\|-b)\quad,\ \psi:\mathbb{R}^3\to\mathbb{R}$$

是半径为b的球面上的均匀分布。其中Dirac delta函数

$$\delta(\vec{r})=(2\pi)^{-d}\int_{\mathbb{R}^d}\exp(i\vec{k}\cdot\vec{r})\,d\vec{k}\quad,\ d\text{是维数}$$

△ 球面上的均匀分布与正态分布的关系：若$\vec{r}$满足半径为b的球面分布，则$r_i/b\sim N(0,1)$，$i=1,2,3$（Muller (1959) Commun. ACM2:19）。这使得许多书以$\vec{r}$在直角坐标轴上的投影的一维随机行走来推算。

△ $\psi(\vec{r})$满足归一化条件：

$$\int_{\mathbb{R}^3}\psi(\vec{r})\,d\vec{r}=\frac{1}{4\pi b^2}\int_{\mathbb{R}^3}\delta(\|\vec{r}\|-b)\,d\vec{r}=\frac{1}{4\pi b^2}\int_{-\infty}^{\infty}dr_1\int_{-\infty}^{\infty}dr_2\int_{-\infty}^{\infty}dr_3\,\delta\left(\sqrt{r_1^2+r_2^2+r_3^2}-b\right)$$

$$=\frac{1}{4\pi b^2}\int_0^\infty\rho^2d\rho\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi\,\delta(\rho-b)$$

$$=\frac{1}{4\pi b^2}\cdot b^2\cdot 2\cdot 2\pi$$

$$=1$$

△ 考虑n个首尾相连、独立满足式(1)的分布的向量$\vec{r}_1,\dots,\vec{r}_n$，记为$\{\vec{r}_i\}$。如此组成的链称为自由结合链（freely jointed chain）。$\vec{r}_i$，$i=1,\dots,n$称链段向量，一组特定的链段向量$\{\vec{r}_i\}$称为自由结合链的一个构象。

△ 自由结合链取构象$\{\vec{r}_i\}$的概率密度是$\Psi(\{\vec{r}_i\})$，它是各个链单向量的联分布

$$\Psi(\{\vec{r}_i\})=\prod_{i=1}^n\psi(\vec{r}_i)$$

$$\int_{\mathbb{R}^{3n}}\Psi(\{\vec{r}_i\})\,d\{\vec{r}_i\}=\prod_{i=1}^n\int_{\mathbb{R}^3}\psi(\vec{r}_i)\,d\vec{r}_i=1$$

△ 自由结合链在某构象$\{\vec{r}_i\}$下的末端位移向量$\vec{R}(\{\vec{r}_i\})=\sum_{i=1}^n\vec{r}_i$，自由结合链的末端位移向量为$\vec{R}$的概率密度是$\Phi(\vec{R})$，它是所有$\{\{\vec{r}_i\}\mid\sum_{i=1}^n\vec{r}_i=\vec{R}\}$的概率之和，即

$$\Phi(\vec{R})=\int_{\mathbb{R}^3}d\vec{r}_1\cdots\int_{\mathbb{R}^3}d\vec{r}_n\,\delta\left(\vec{R}-\sum_{i=1}^n\vec{r}_i\right)\Psi(\{\vec{r}_i\})$$

$$=\int_{\mathbb{R}^3}d\vec{r}_1\cdots\int_{\mathbb{R}^3}d\vec{r}_n\,\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{k}\,\exp\left[i\vec{k}\cdot\left(\vec{R}-\sum_{i=1}^n\vec{r}_i\right)\right]\psi(\vec{r}_1)\cdots\psi(\vec{r}_n)$$

$$=\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{r}_1\cdots\int_{\mathbb{R}^3}d\vec{r}_n\int_{\mathbb{R}^3}e^{i\vec{k}\cdot\vec{R}}\prod_{i=1}^n e^{-i\vec{k}\cdot\vec{r}_i}\psi(\vec{r}_i)\,d\vec{k}$$

$$=\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{k}\,e^{i\vec{k}\cdot\vec{R}}\prod_{i=1}^n\int_{\mathbb{R}^3}d\vec{r}_i\,e^{-i\vec{k}\cdot\vec{r}_i}\psi(\vec{r}_i)$$

$$=\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{k}\,e^{i\vec{k}\cdot\vec{R}}\left[\int_{\mathbb{R}^3}d\vec{r}\,e^{-i\vec{k}\cdot\vec{r}}\psi(\vec{r})\right]^n$$

其中

$$\int_{\mathbb{R}^3}d\vec{r}\,e^{-i\vec{k}\cdot\vec{r}}\psi(\vec{r})=\frac{1}{4\pi b^2}\int_0^\infty\rho^2d\rho\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi\,e^{-i\|\vec{k}\|\rho\cos\theta}\delta(\rho-b)$$

$$=\frac{1}{4\pi b^2}\cdot\frac{4\pi b\sin(kb)}{k}$$

$$=\frac{\sin(kb)}{kb}$$

$$\therefore\ \Phi(\vec{R})=\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{k}\,e^{i\vec{k}\cdot\vec{R}}\left(\frac{\sin(kb)}{kb}\right)^n$$

△ $kb\ll1$的近似

由 $\sin x/x=1-\frac{x^2}{6}+o(x^3)$，$x\to0$，$[\sin(kb)/(kb)]^n\simeq\left(1-\frac{k^2b^2}{6}\right)^n$，$kb\ll1$

又由 $\exp(-x)=1-x+o(x^2)$，$x\to0$，$\exp\left(-\frac{1}{6}k^2b^2\right)\simeq1-\frac{1}{6}k^2b^2$，$kb\ll1$

$$\therefore\quad[\sin(kb)/(kb)]^n\simeq\exp\left(-\frac{1}{6}nk^2b^2\right)$$

$$\Phi(\vec{R})\approx\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}d\vec{k}\,e^{i\vec{k}\cdot\vec{R}}\,e^{-nk^2b^2/6}$$

$$=\frac{1}{(2\pi)^3}\prod_{i=1}^3\int_{-\infty}^{\infty}dk_i\,e^{ik_iR_i-nk_i^2b^2/6}$$

$$=\frac{1}{(2\pi)^3}\prod_{i=1}^3\sqrt{\frac{6\pi}{nb^2}}\exp\left(-\frac{3R_i^2}{2nb^2}\right)$$

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

近似了的$\Phi(\vec{R})$满足归一化条件。

△ 特别地，由近似式，$\langle\|\vec{R}\|^2\rangle=nb^2$，$kb\ll1$.

△ $kb\ll1$可翻译成$n\gg1$，即当我们关心的相关尺度远大于链段时，即链长很大。

△ 事实上，由中心极限定理，无穷多个任意分布的随机量之和的分布是正态分布。

球坐标系：

$$\begin{cases}x=\rho\sin\theta\cos\varphi & \rho>0,\ 0<\theta\leq\pi,\ 0<\varphi<2\pi\\ y=\rho\sin\theta\sin\varphi\\ z=\rho\cos\theta\end{cases}$$

$$J=\begin{pmatrix}\sin\theta\cos\varphi & \rho\cos\theta\cos\varphi & -\rho\sin\theta\sin\varphi\\ \sin\theta\sin\varphi & \rho\cos\theta\sin\varphi & \rho\sin\theta\cos\varphi\\ \cos\theta & -\rho\sin\theta & 0\end{pmatrix}$$

$\vec{C}_1=(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta)^T$

$\vec{C}_2=(\rho\cos\theta\cos\varphi,\rho\cos\theta\sin\varphi,-\rho\sin\theta)^T$

$\vec{C}_3=(-\rho\sin\theta\sin\varphi,\rho\sin\theta\cos\varphi,0)^T$

$h_1=1,\ h_2=\rho,\ h_3=\rho\sin\theta$

$$\begin{cases}x^c= x\sin\theta\cos\varphi+y\sin\theta\sin\varphi+z\cos\theta=\sqrt{x^2+y^2+z^2}\\ y^c= x\cos\theta\cos\varphi+y\cos\theta\sin\varphi-z\sin\theta=0\\ z^c= -x\sin\varphi+y\cos\varphi=0\end{cases}$$

注意 一般地，点$\vec{r}=r_\rho\hat{\rho}+r_\theta\hat{\theta}+r_\varphi\hat{\varphi}$的基$\hat{\rho},\hat{\theta},\hat{\varphi}$依赖$\vec{r}$，故

$$\vec{k}=k_\rho\hat{\rho}(\vec{k})\ ,\ \vec{r}=r_\rho\hat{\rho}(\vec{r}),$$

$$\vec{k}\cdot\vec{r}=k_\rho r_\rho\,\hat{\rho}(\vec{k})\cdot\hat{\rho}(\vec{r})$$

$$=k_\rho r_\rho(\sin\theta_k\cos\varphi_k\sin\theta_r\cos\varphi_r+\sin\theta_k\sin\varphi_k\sin\theta_r\sin\varphi_r+\cos\theta_k\cos\theta_r)$$

$$=k_\rho r_\rho[\sin\theta_k\sin\theta_r\cos(\varphi_k-\varphi_r)+\cos\theta_k\cos\theta_r]$$

$$=k_\rho r_\rho\cos\omega,\quad \omega\text{是}\vec{k}\text{与}\vec{r}\text{的夹角}$$

如果在整个$\mathbb{R}^3$上的关于$\vec{r}$的积分含$\vec{k}\cdot\vec{r}$，在球坐标下$\vec{k}\cdot\vec{r}=\|\vec{k}\|\|\vec{r}\|\cos\omega$，其中当$\theta$遍历$(0,\pi]$，$\varphi$遍历$(0,2\pi]$，则$\omega$遍历了$(0,\pi]$，积分可使$\omega=\theta$而保持原值。有些书的表述是：（在积分时）不妨设$\vec{k}$与z轴方向相同。