第一章　导　论

- 高分子科学的重要性
- 高分子的特点
- 高分子物理的研究内容和重要性
- 高分子物理的发展简史
- 本课程所讲授的内容

1. 高分子科学的重要性

- 现代工业的重要标志
- 其他产业的重要支柱…

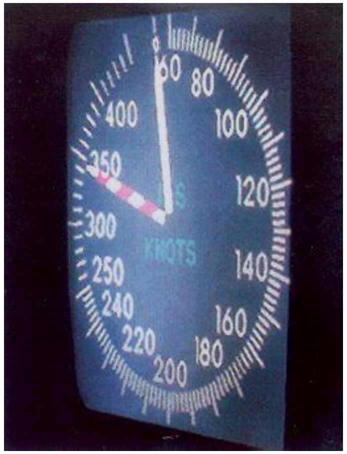
"I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect on everyday life. The world would be a totally different place without artificial fibers* (纤维)*, plastics* (塑料)*, elastomers* (弹性体)*, etc. Even in the field of electronics, what would you do without insulation? And there you come back to polymers again."

Lord Todd, president of the Royal Society of London, quoted in *Chem. Eng. News* **1980,** *58*(*40*), 29, in answer to the question, What do you think has been chemistry's biggest contribution to science, to society?

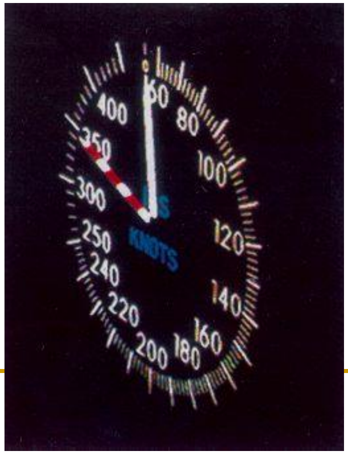
Polymers Related to Information Technology

- **LCD after using polymer optical compensation films:**

Color degradation and narrow viewing angle without negative compensation films

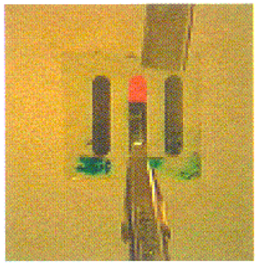


High contrast ratio and wide viewing angle with negative compensation films



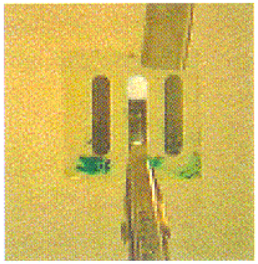
- **Polymer light emitting diodes:**

Red



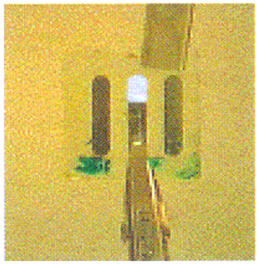
Voltage: 5V

Yellow



Voltage: 10V

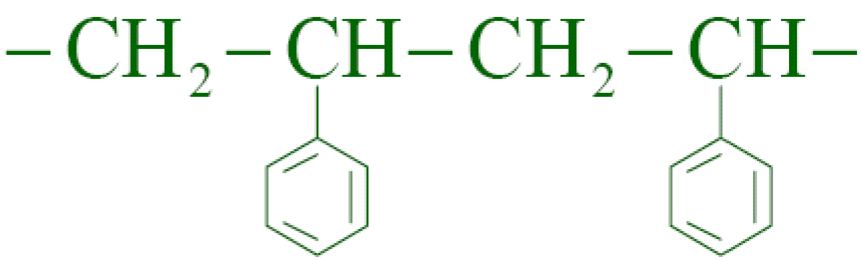
Blue



Voltage: 20V

2. 高分子的特点

(1) 长链分子



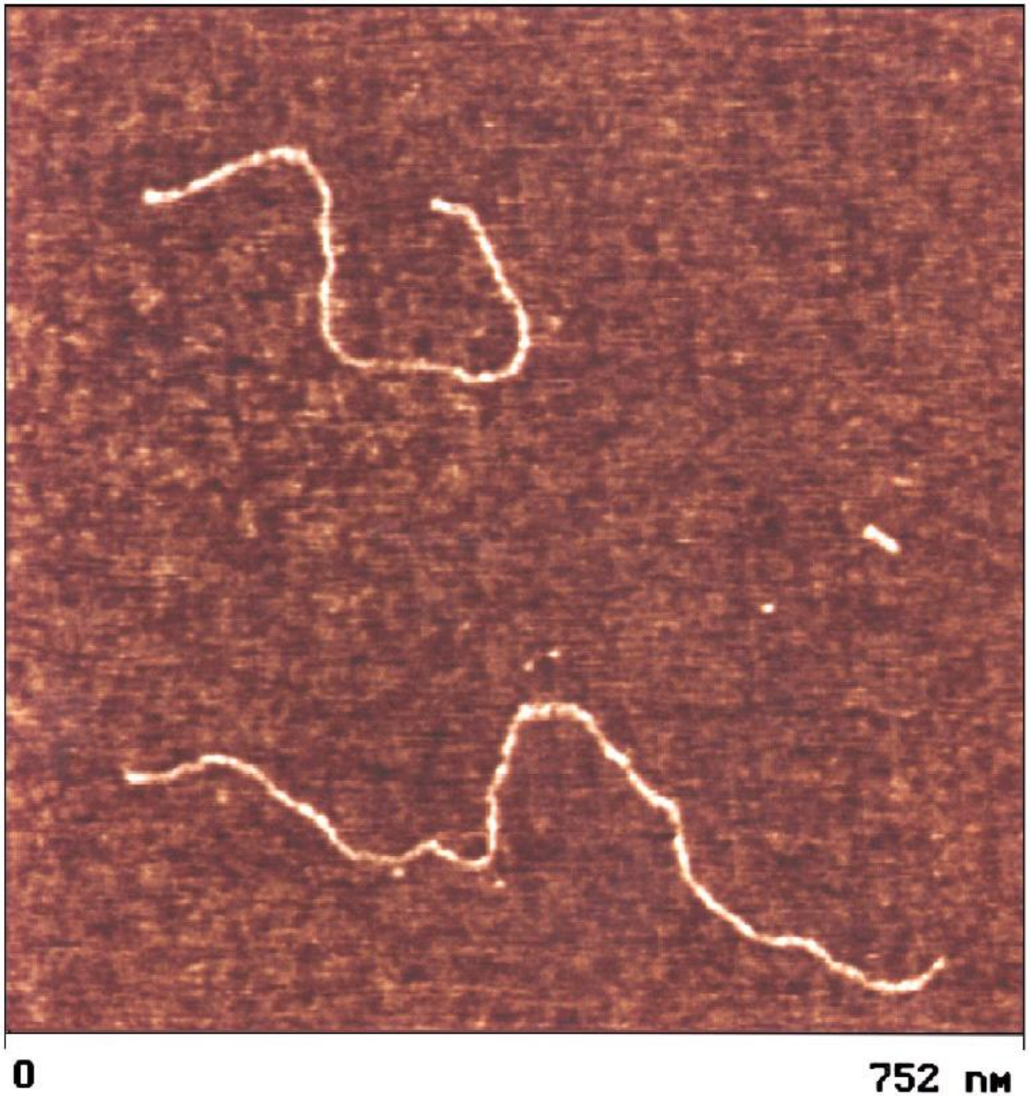
Poly(styrene)

***N*>>1**

合成高分子*N*~10^2-10^4

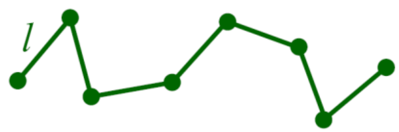
天然高分子*N*~10^9-10^{10} DNA、RNA，Protein,…

AFM of Single Chains



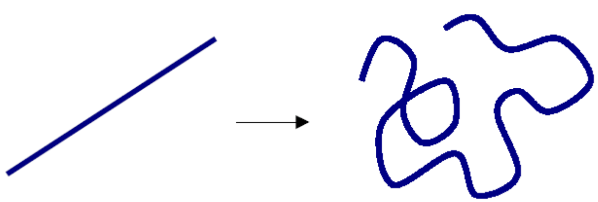
长链分子的主要特点

a. 单体连接->缺少独立运动的自由度->熵的损失 & 又存在巨大的构象熵



b. 可具有复杂的拓扑结构

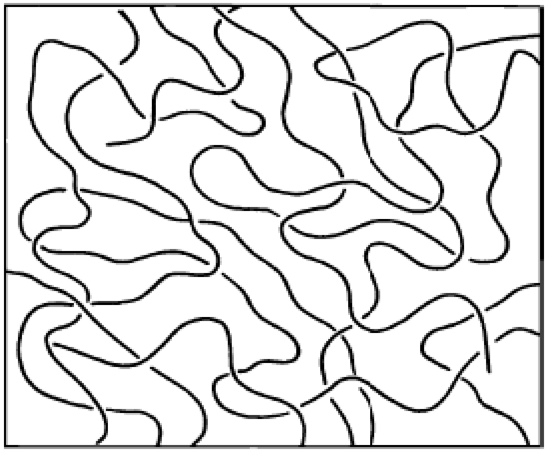
c. 高分子链具有不同程度的柔顺性



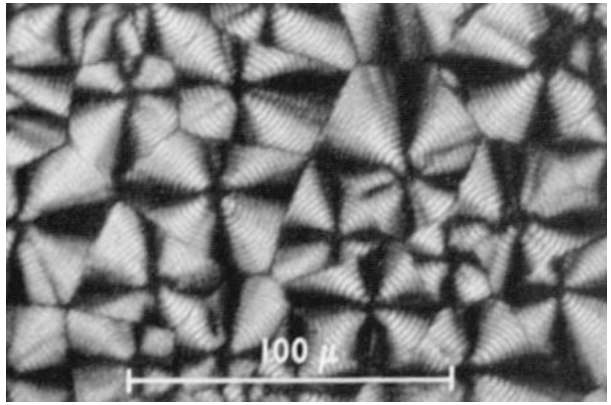
d. 链间有缠结

e. 大跨度的松弛时间谱

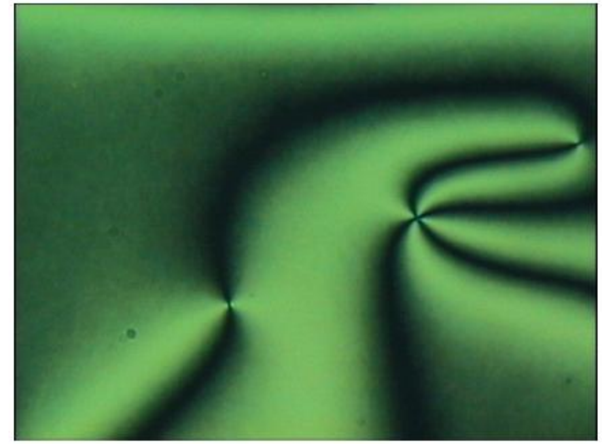
(2) 结构和性能的多层次和多变性



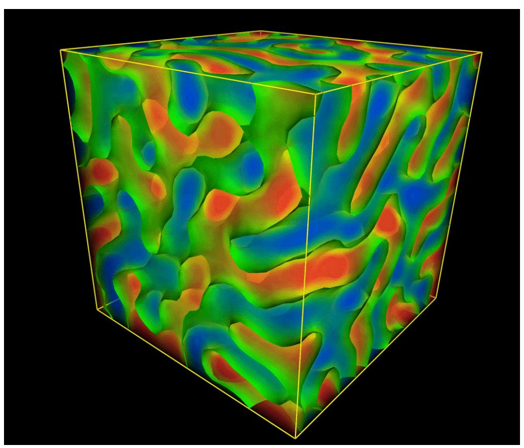
Amorphous & Melt



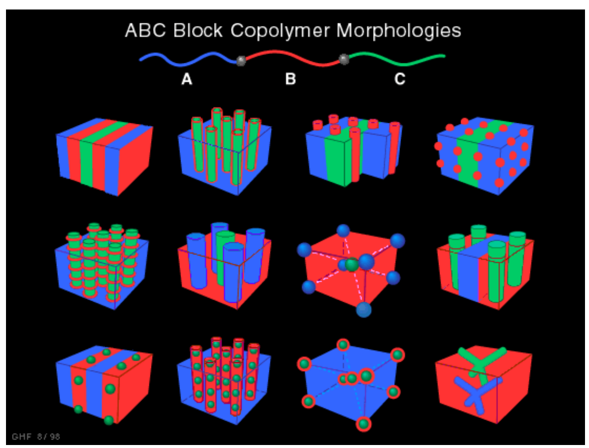
Crystal



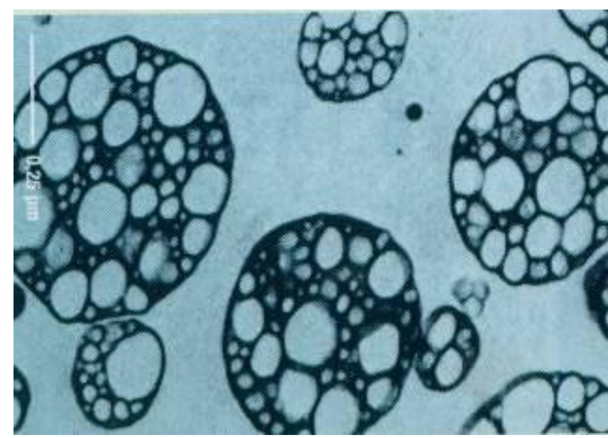
Liquid Crystal



Blend



Triblock Copolymer



HIPS & ABS

(3) 结构、性能与时温的依赖性

分子运动多层次

不同温度下的分子运动行为不同

不同时间尺度观察的性质不同

时温等效原理

3. 高分子物理的研究内容和重要性

(1) 研究内容

分子运动

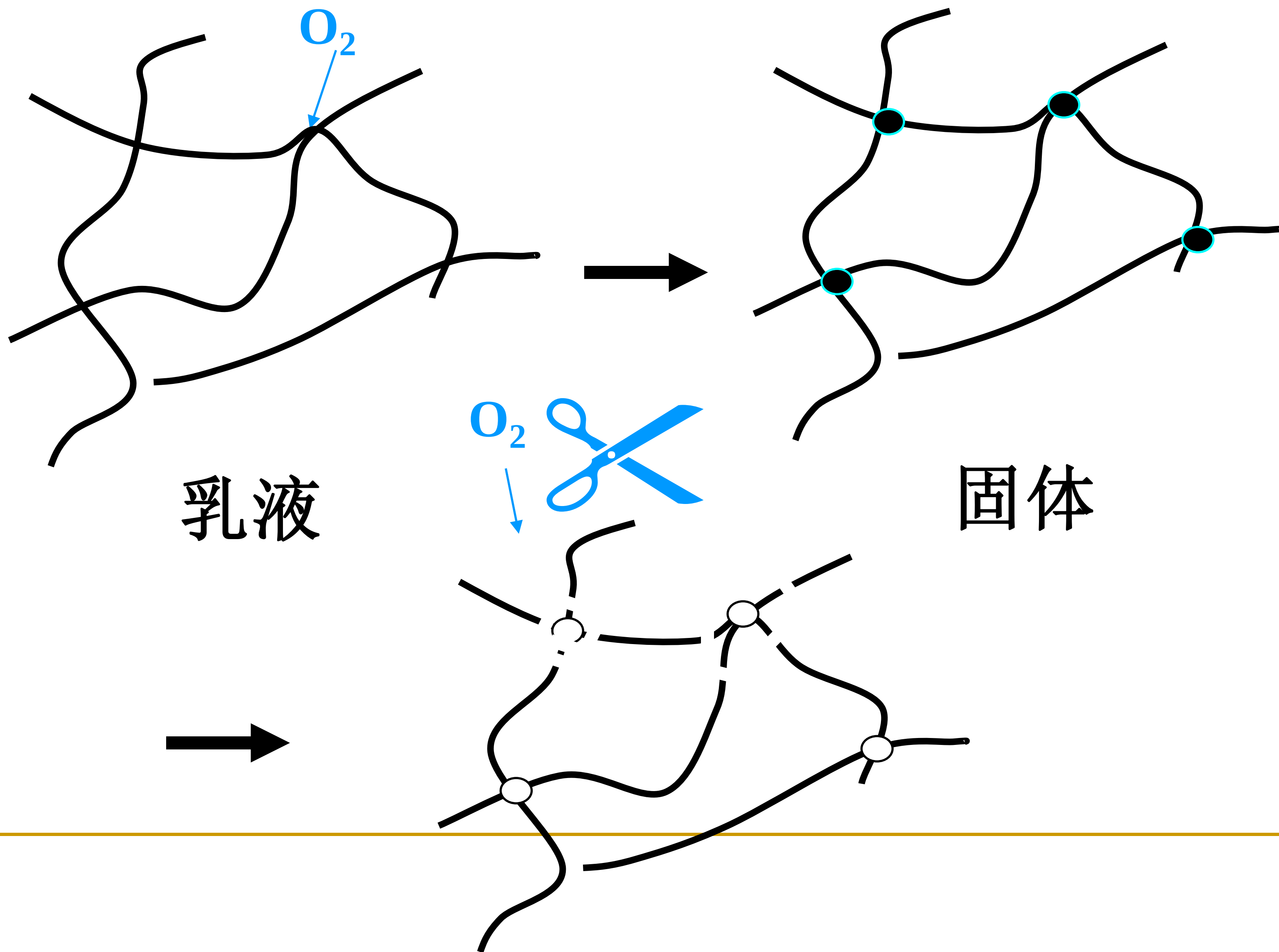
结构 ⟷ 性能

包括：理论、实验表征等手段

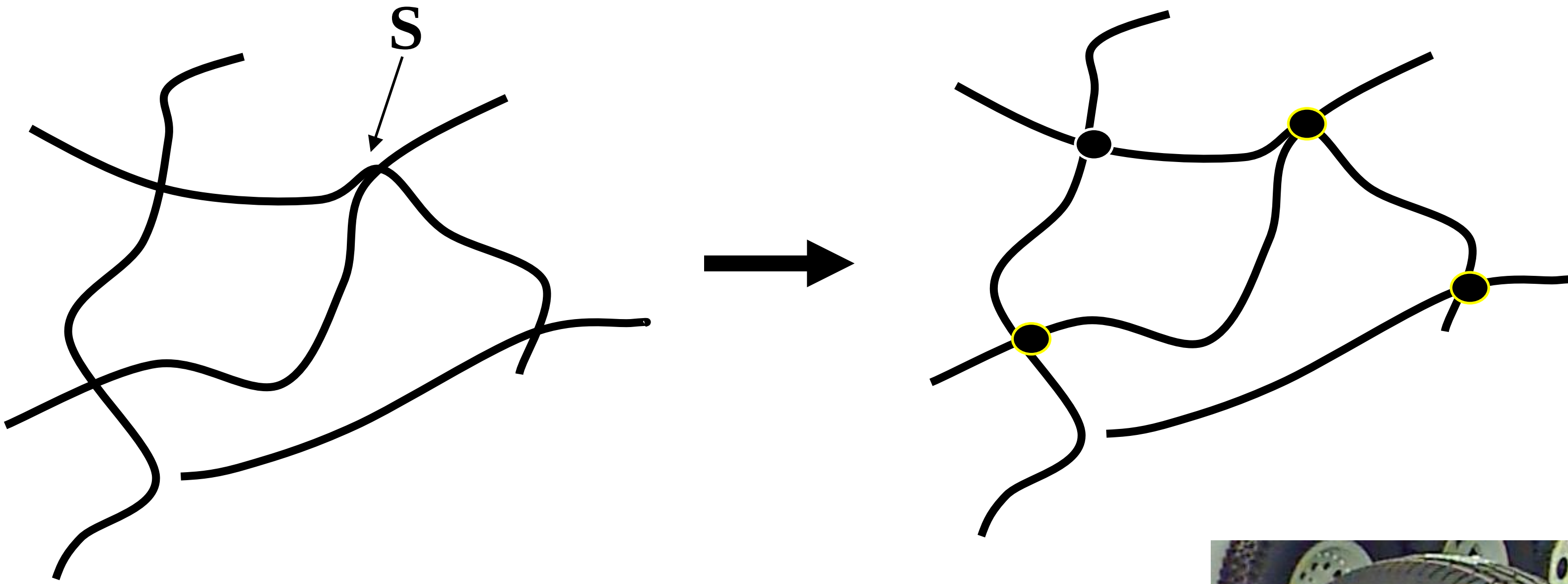
建立一个普适性的理论架构

为高分子材料的分子、结构设计和性能设计提供理论基础

(2) 重要性-a.从印第安人穿的靴子谈起



1839年Goodyear的硫化技术



硫化橡胶

不了解结构特点，就要走很多的弯路，
更谈不上分子设计

(2) 重要性-b.著名公司的材料研发流程

市场调研

高分子物理-设计-理论分析

结构性能表征

高分子化学-合成,改性

高分子产品

4. 高分子物理的发展简史

高分子结构的发现 Staudinger 1920-1930

1. 高分子物理的起点

橡胶弹性的分子理论 **Kuhn, Mark 1930-1935**

高分子链构象统计理论

2. 高分子的物化时代和**DNA**的发现 **1935-1965**

Flory 溶液理论，**Rouse-Zimm**链动力学理论

Watson-Crick的**d-Helix DNA, Natta**聚烯烃

聚集态结构表征方法

4. 高分子物理的发展简史

3. 现代物理向高分子物理的渗透 1965-

de Gennes 和 Edwards的蛇行(reptation)理论, 标度概念(scaling concept)

高分子物理已成为现代凝聚态物理的重要分支-软凝聚态物理(soft condensed matter)、软物质(soft matter)或复杂流体(complex fluids)

5. 本课程讲授的内容

结构

(1) 高分子的形状和大小

构型和构造　　一级(近程)结构

构象　　二级(远程)结构

分子量和分子量分布

(2) 高分子溶液, 高分子共混物, 嵌段共聚物

稀溶液->亚浓溶液->浓溶液的热力学

(3) 高分子的聚集态结构　　三级结构

非晶态、结晶态和液晶态

5. 本课程讲授的内容

(4) 高分子的分子运动学

高分子的三态：玻璃态、高弹态、粘流态

玻璃化转变

性能

(5) 高分子的力学性能

小应变下的橡胶弹性理论、粘弹性

大应变下的强度与破坏

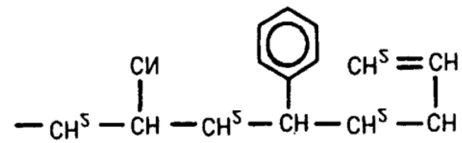
(6) 高分子的电学性质

参考书

- 高分子物理(修订版&第三版，复旦大学出版社，1990&2007 , 何曼君 陈维孝 董西霞编)
- 高聚物的结构与性能(中科大，科学出版社)
- 聚合物的结构和物理性质(李斌才,科学出版社)
- **The Physics of Polymers (2nd Edition) (Springer, 1997, G. R. Strobl)**
- **Introduction to Polymer Physics (Oxford,1995, M. Doi)**
- **Polymer Physics (Cambridge, 2003, Rubinstein)**
- **Introduction to Physical Polymer Science (Wiley, 2006, L. Sperling)**
- **Principles of Polymer Chemistry (Flory)**
- 聚合物科学与材料(科学出版社，**Mark, Tobolsky et. al.)**

第二章 高分子的大小和形状

➢ **Primary (一级):**



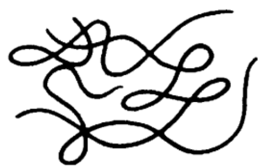
➢ **Secondary (二级):**

Random coil

Folded chain

Spiraled chain (helix)

➢ **Tertiary (三级):**



Spaghetti structure

Fringed micelle

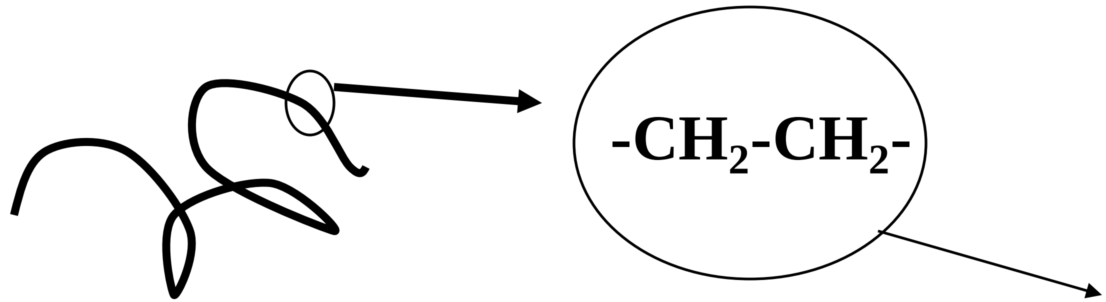
Over spiraling (superhelix)

➢ **Quaternary (四级):**

Spherulite

第二章 高分子的大小和形状

2.1 近程结构 (local)



局部的化学结构

2.1.1 构造 (Constitutions or Architectures)

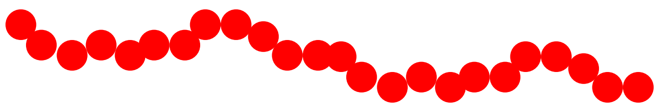
2.1.1.1 结构单元的化学组成

2.1.1.2 键接结构

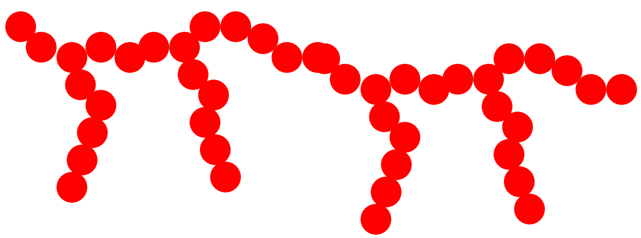
2.1.1.3 支化与交联

2.1.1.4 均聚与共聚

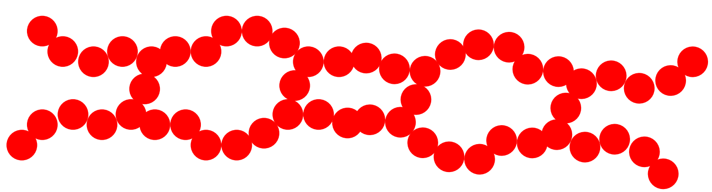
- **Homopolymers (均聚物):**



Linear polymer

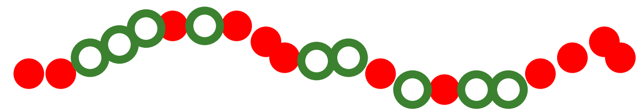


Branched polymer

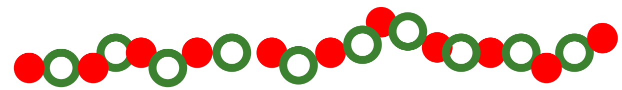


Cross-linked polymer

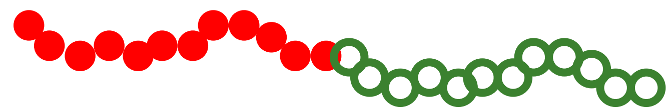
- **Copolymers (共聚物):**



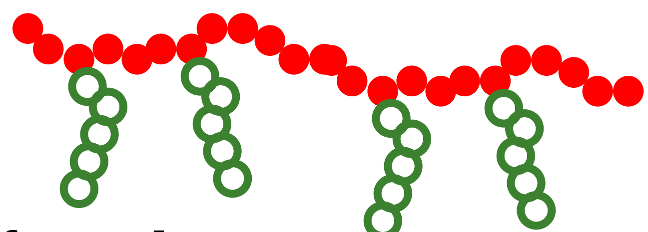
Linear random copolymer



Linear alternating copolymer



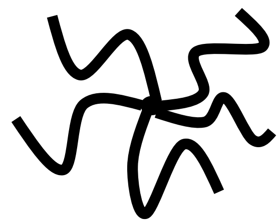
Linear block copolymer



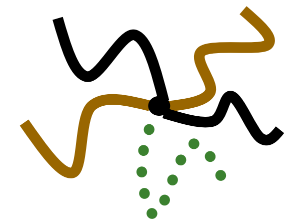
Graft copolymer

星形和超支化高分子

- **Star (星状) polymers**



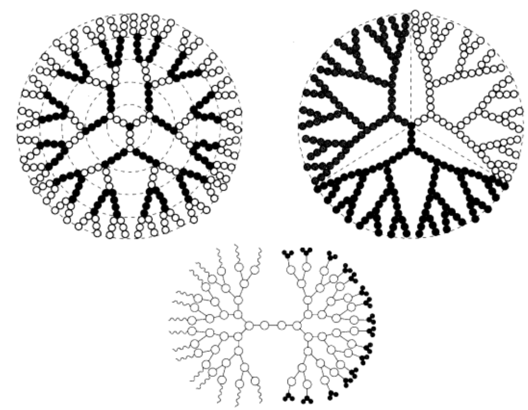
homo-armed (同臂)



hetro-armed (杂臂)

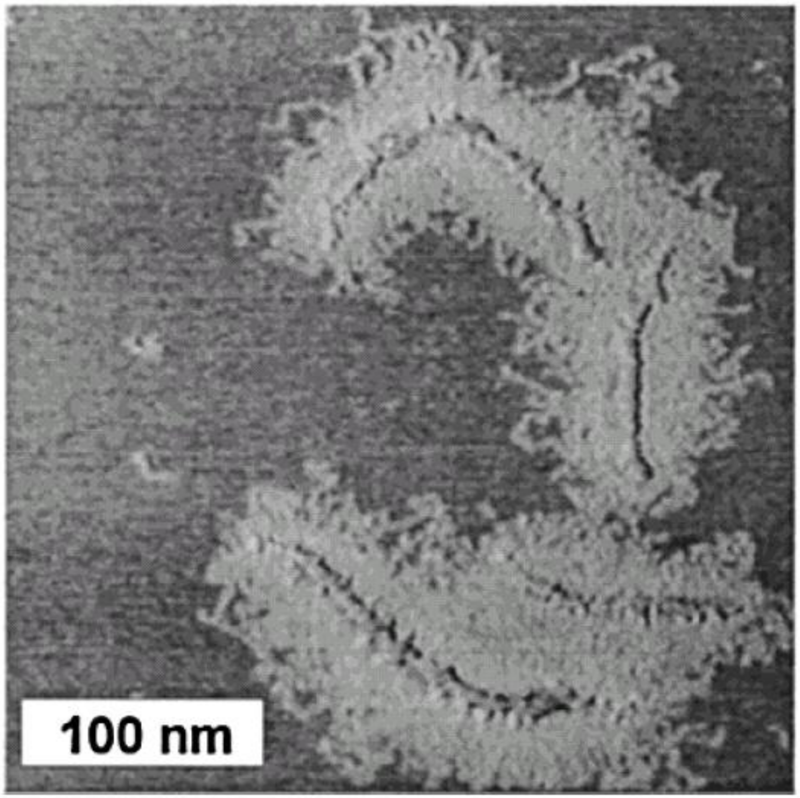
- **Hyperbranched (超枝化) Polymers and Dendrimers (树枝链):**

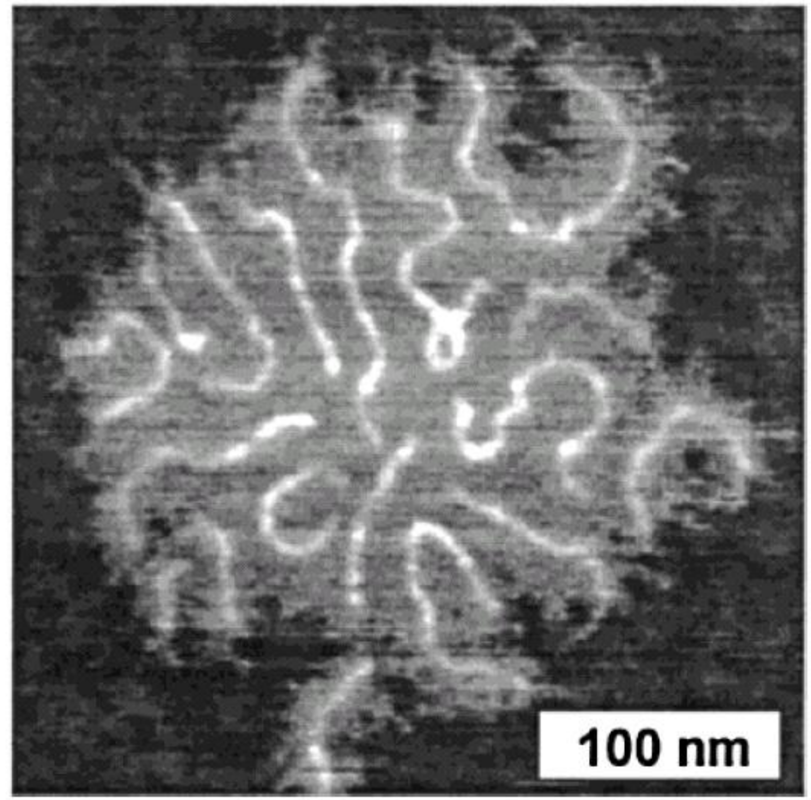
The composition of dendrimers can be varied throughout the molecule in a systematic way



- **How many different architectures of macromolecules can you imagine?**

AFM of branched Polymers

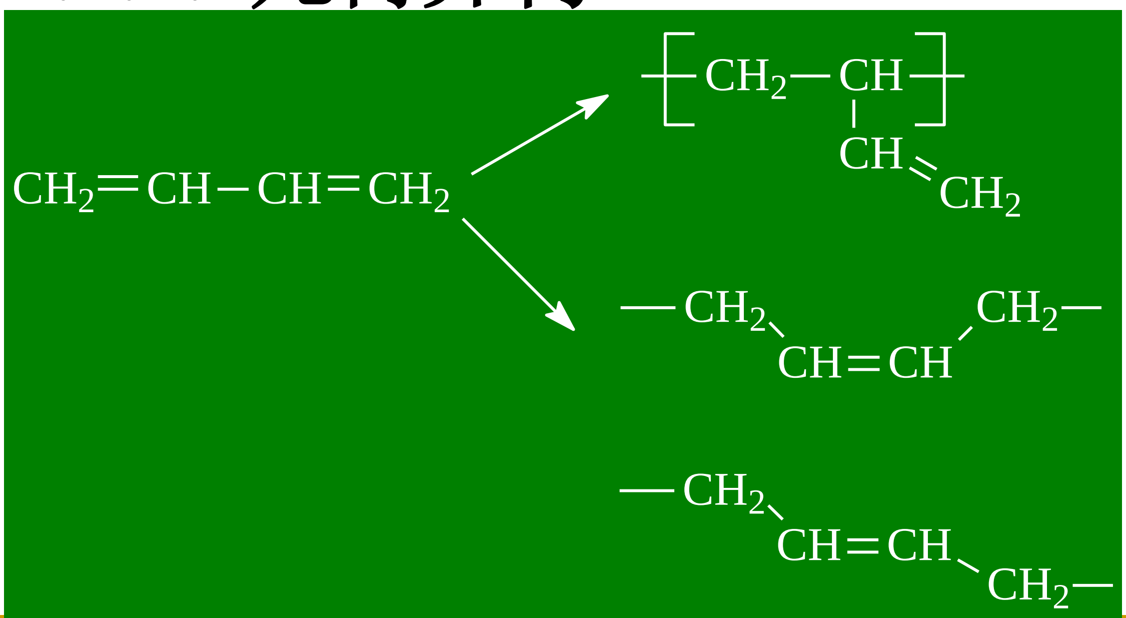




2.1.2 构型(Configurations)

Arrangements fixed by the chemical bonding in the molecule, such as *cis* (顺式) and *trans* (反式), *isotactic* (等规) and *syndiotactic* (间规) **isomers**. The *configuration* of a polymer **cannot be altered** unless chemical bonds are broken and reformed.

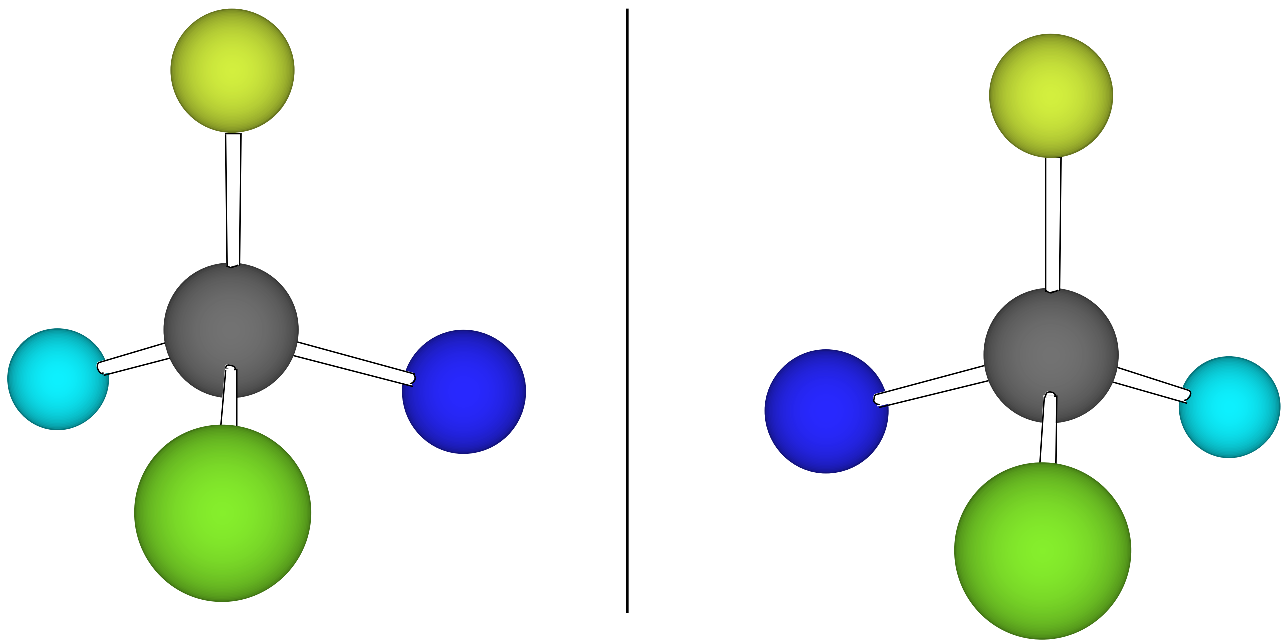
2.1.2.1几何异构



顺式*cis*

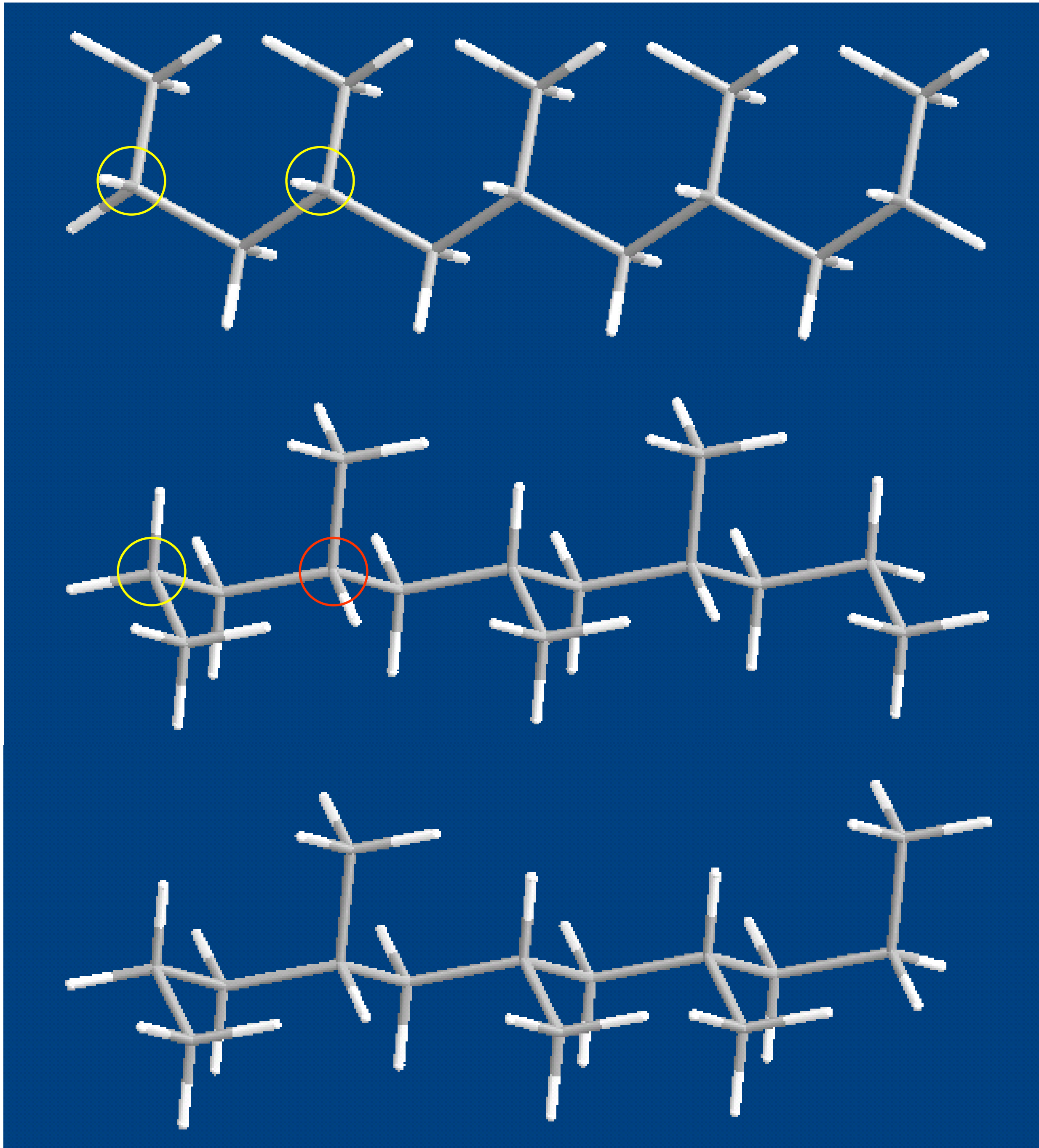
反式*trans*

2.1.2.2 旋光异构



手性分子

问题:一根链中同时出现不同的C*??



全同
等规*isotactic*

间同
间规*syndiotactic*

无规*atactic* or *block*

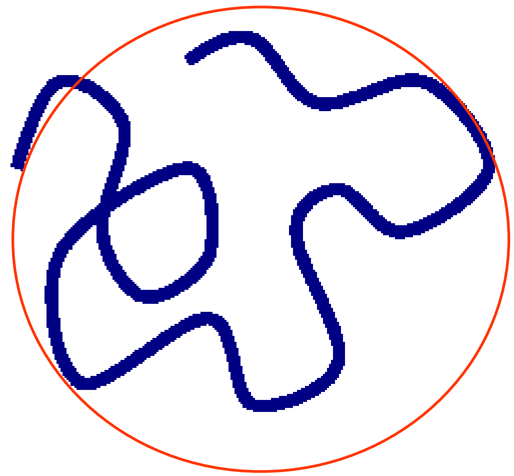
2.1.2 构型(Configurations)

化学键固定的原子在空间的几何排列

改变构型(顺反和旋光)必须打断化学键!!!

2.2 远程结构 (glouble)

一根链整体的形状和大小



2.2.1 高分子链的质量

长度平均-数均分子量(number averaged)

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum w_i}{\sum \frac{w_i}{M_i}} = \frac{\int n(M) M dM}{\int n(M) dM} = \frac{\int w(M) dM}{\int \frac{w(M)}{M} dM}$$

重量平均-重均分子量(weight averaged)

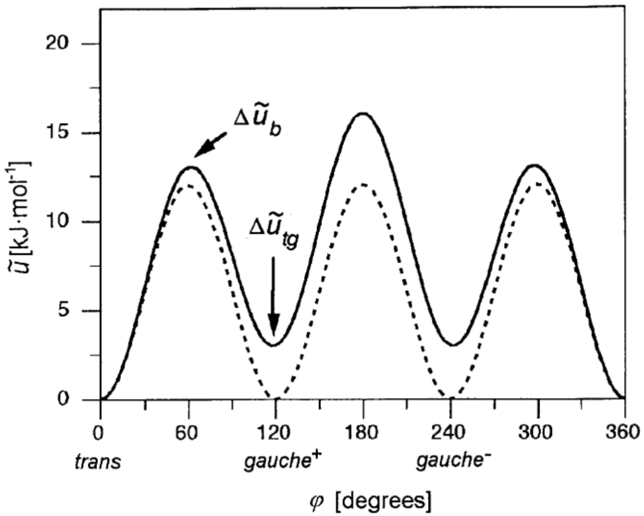
$$M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\int w(M) M dM}{\int w(M) dM} = \frac{\int n(M) M^2 dM}{\int n(M) M dM}$$

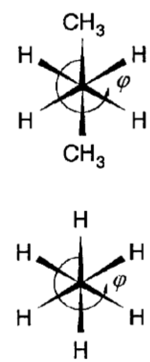
分子量分布

$$f(n_i) = \frac{n_i}{\sum_i n_i} \qquad F(w_i) = \frac{w_i}{\sum_i w_i}$$

2.2.2 高分子的内旋转构象

➢ ***trans* (反式) and *gauche* (旁式) conformations:**





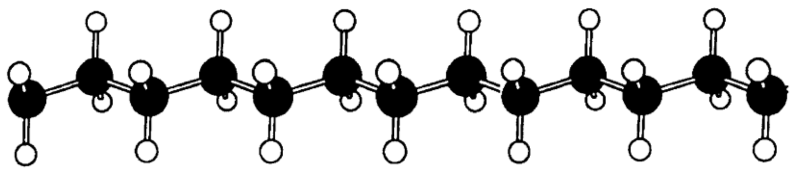
Potential energies associated with the rotation of central C-C-bond for ethane (*dashed line*) and butane (*solid line*). The sketches show the two molecules in views along the C-C-bond.

Rotational Isomeric States (旋转异构态RIS) – 无需打断化学键

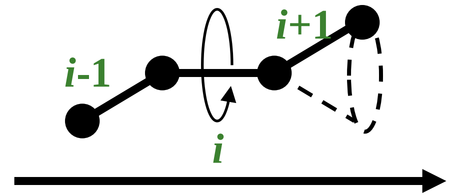
假设每个单元有2个旋转异构态 ⟶ 一根链的异构态数目将达2^{N-3}

Random coil (无规线团) of polymer

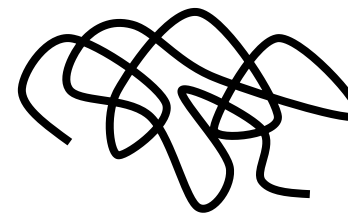
- 基本的链构象



Zigzag conformation of PE (2_1 helix)

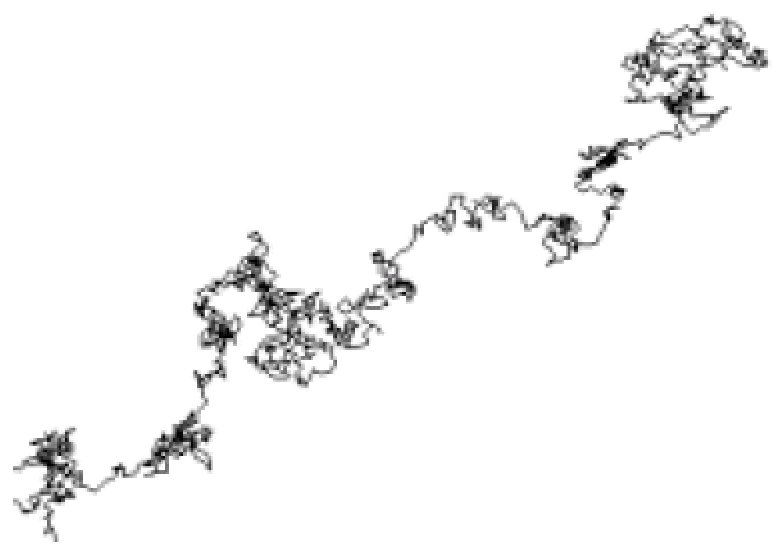


In melt or solution



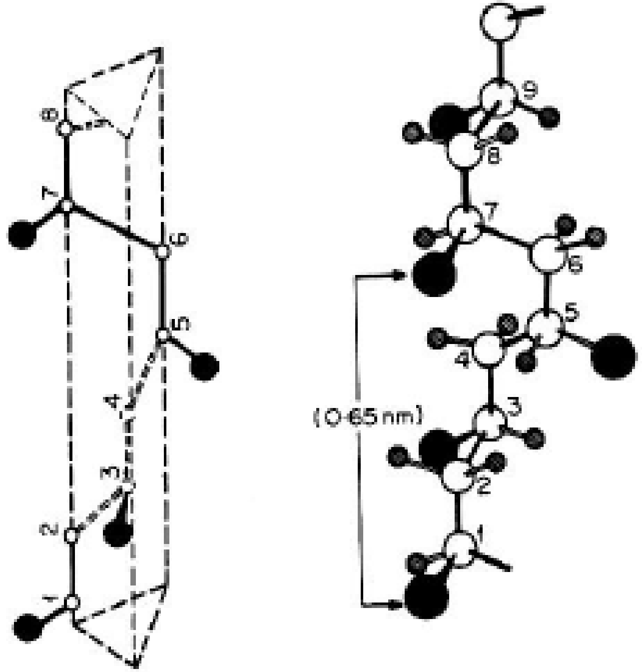
Random coil
无规线团

Computer Simulation of a Single Chain in Solutions

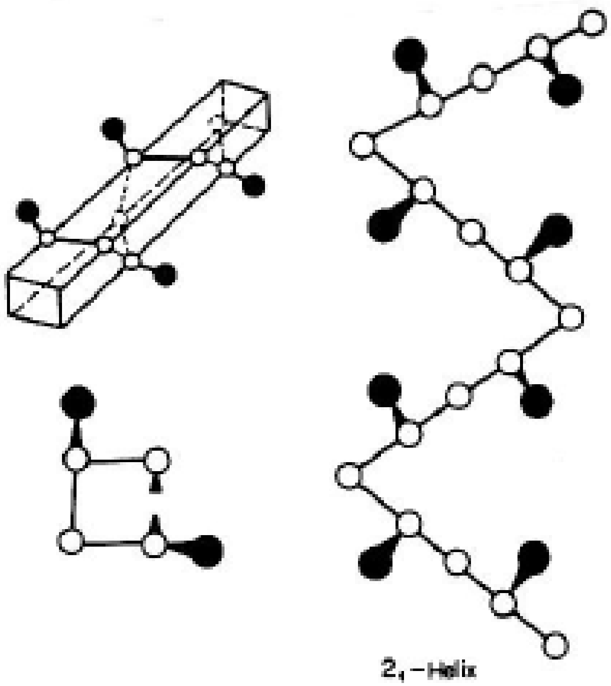


特殊的链构象：平面锯齿链(zigzag)和螺旋链

it-PP



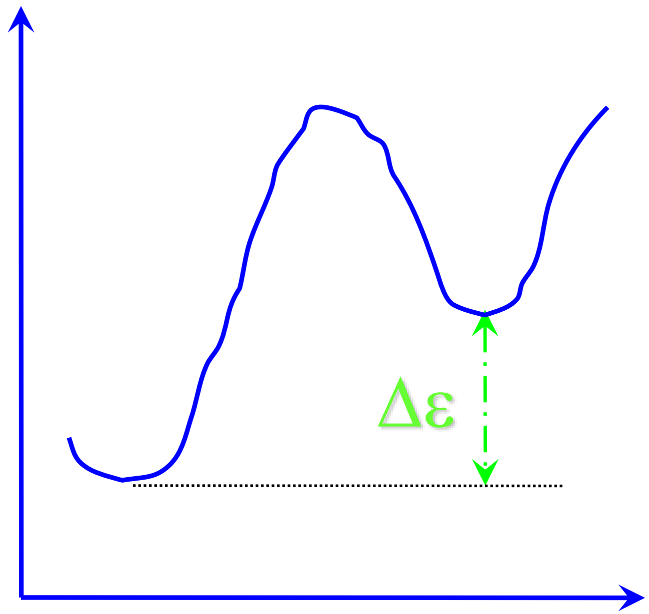
s-PP



Polyproplenes in Crystals

2.2.3 高分子的柔顺性(flexibility)

2.2.3.1 静态柔顺性—热力学定义



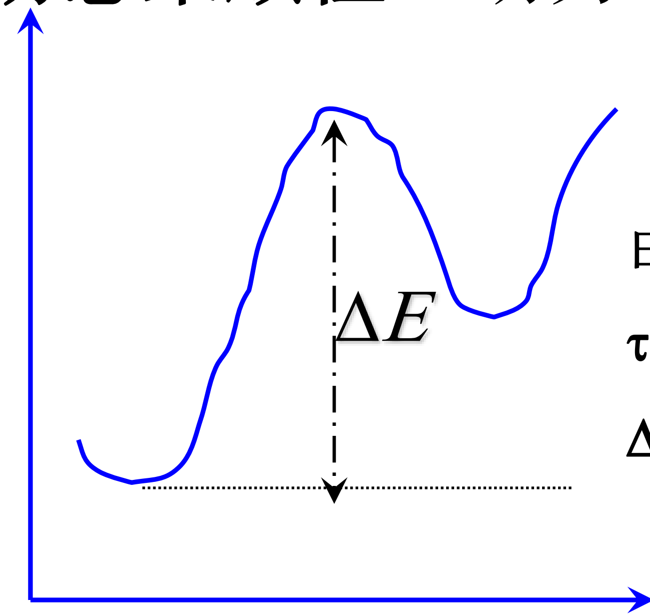
持久长度

$l_p = l\exp(\Delta\varepsilon/kT)$

$\Delta\varepsilon \to 0,\ l_p \to l$

2.2.3 高分子的柔顺性(flexibility)

2.2.3.2 动态柔顺性—动力学定义



由1到2的转换时间(持续时间)

$\tau_p = \tau_1 \exp(\Delta E/kT)$

$\Delta E \to 0,\ \tau_p \to \tau_1$

2.2.3.3 影响柔顺性的主要因素

主链结构

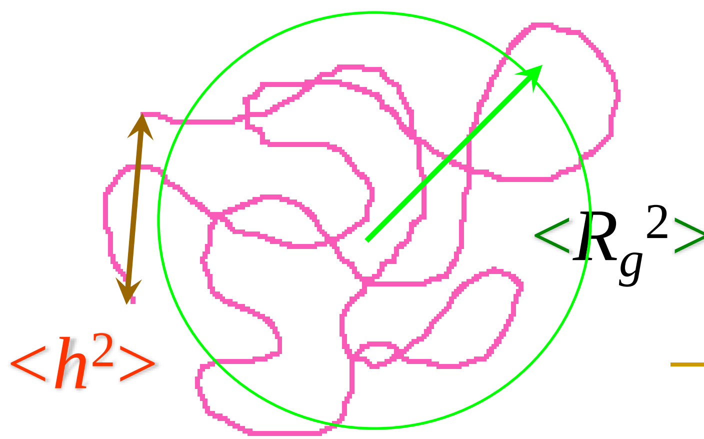
侧基

链的长短

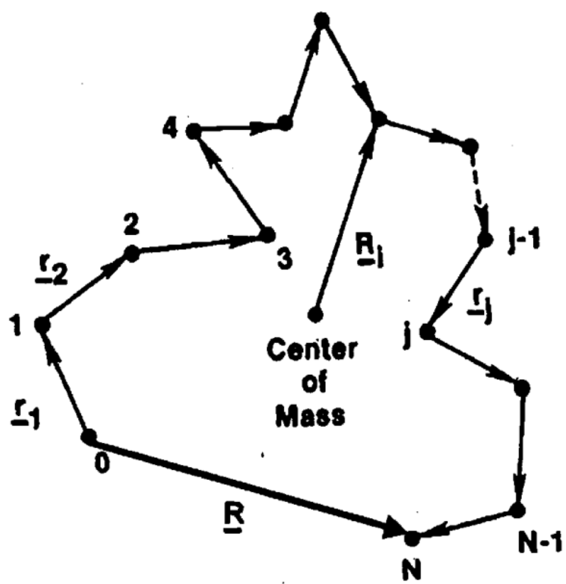
2.2.4 高分子链构象的统计

关键是寻找无规线团状柔性链的表征参量

2.2.4.1 均方末端距$\langle h^2\rangle$和均方回转半径$\langle R_g^2\rangle$的几何统计方法



$<h^2>$和$<S^2>$的定义



Schematic representation of homopolymer chain of N+1 mass points and N bond vectors.

- End-to-end vector (末端距矢量):

$$\vec{R} \equiv \sum_{i=1}^{N} \vec{r}_i \qquad <h>=<\overrightarrow{R}>=0$$

- Mean-squared end-to-end distance (均方末端距):

$$\left\langle h^2 \right\rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} r_i \cdot r_j \right\rangle$$

- Mean-squared radius of gyration (homopolymer chain) (均方回转半径):

$$\left\langle R_g^2 \right\rangle \equiv \left\langle \frac{\sum_{i=0}^{N} m_i R_i^2}{\sum_{i=0}^{N} m_i} \right\rangle$$

m_i: mass of each point

R_i: vector from the common center of mass to i-point

理想高分子链模型的均方末端距<h^2>

每根键长相等，键的数目为N，不是聚合度!!!

$$\boldsymbol{h} = \boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3 + \ldots + \boldsymbol{r}_{N-1} + \boldsymbol{r}_N \longrightarrow h^2 = \sum_{i=1}^{N} \boldsymbol{r}_i \sum_{j=1}^{N} \boldsymbol{r}_j = \sum_{i=1}^{N} \boldsymbol{r}_i^2 + 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j$$

$$\boldsymbol{r}_i = l \cdot \boldsymbol{e}_i$$

l: the bond length

e_i: the unit vector

$$\langle h^2 \rangle = Nl^2 + 2\left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle = Nl^2 + 2l^2 \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \boldsymbol{e}_i \cdot \boldsymbol{e}_j \right\rangle$$

$$\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \cos\theta_{ij}$$

$$\langle h^2 \rangle = Nl^2 + 2l^2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \cos\theta_{ij} \rangle$$

(1)自由连接

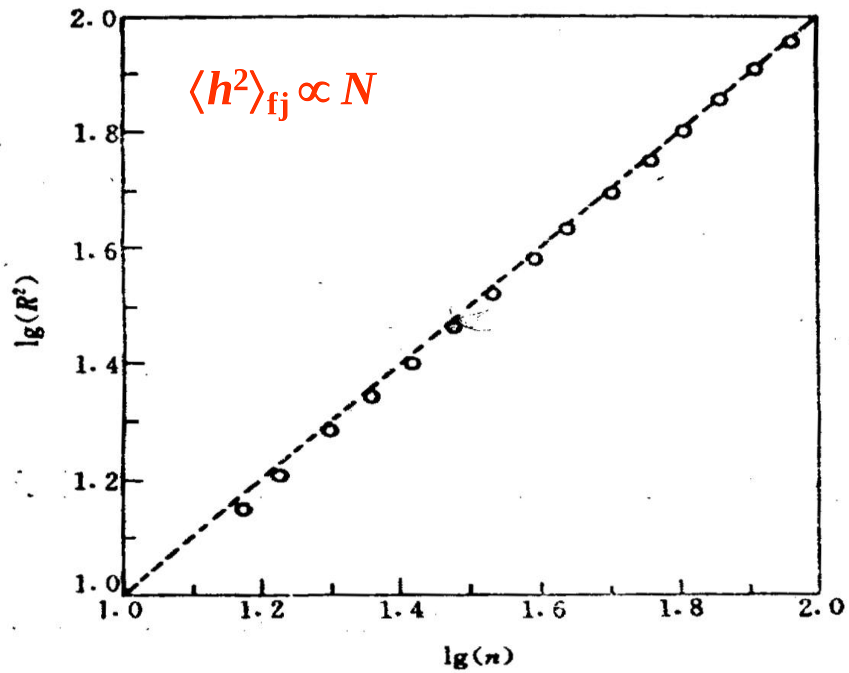
(2) 自由旋转

(1) 自由连接(freely-jointed)链的<h^2>

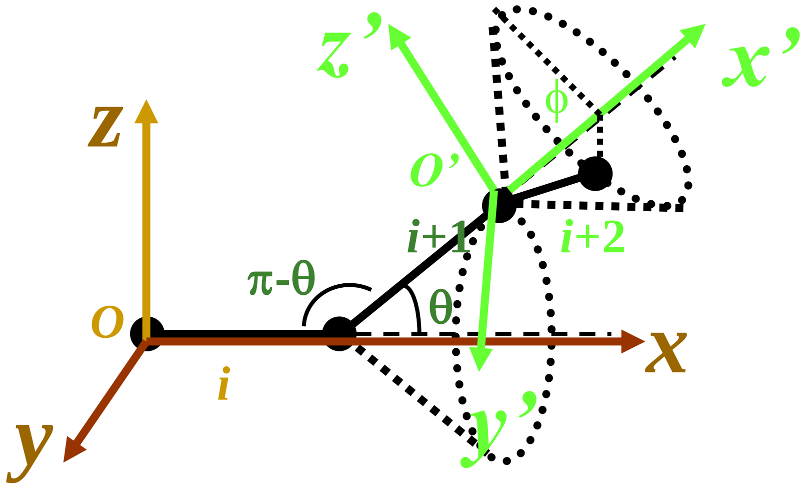
θ_{ij} ~ 0-180　　$\langle \cos\theta_{ij} \rangle = 0$

$$\langle h^2 \rangle_{\text{fj}} = Nl^2 + 2l^2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \cos\theta_{ij} \rangle = \underline{Nl^2}$$

既有分子量的特征，又有局部化学结构的特点



(2) 自由旋转(freely-rotating)链的$<h^2>$



*O'y'*垂直纸面, *O'z'*平行纸面

	$O'x'$	$O'y'$	$O'z'$
Ox	$\cos\theta$	0	$\cos(\pi/2+\theta)$
Oy	0	1	0
Oz	$\sin\theta$	0	$\cos\theta$

相邻两键的θ角是固定的

$$\langle e_i \cdot e_{i\pm1} \rangle = \cos\theta$$

例：

$$e_{i+2} = \begin{pmatrix} \cos\theta & 0 & \cos(\pi/2+\theta) \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta\cos\phi \\ \sin\theta\sin\phi \end{pmatrix}$$

$$\langle e_i \cdot e_{i\pm2} \rangle = \cos^2\theta$$

$$\langle e_i \cdot e_{i\pm m} \rangle = \cos^m\theta$$

$$e_i = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix}$$

$$\langle e_i \cdot e_j \rangle = \cos^{|i-j|}\theta$$

$$\langle e_i \cdot e_{i\pm2} \rangle = \cos^2\theta - \sin^2\theta \langle \sin\phi \rangle$$

自由旋转(freely-rotating)链的<h^2>

$$
\begin{aligned}
&2l^2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left\langle \cos\theta_{ij}\right\rangle \\
&=2l^2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left\langle e_i e_j\right\rangle
\end{aligned}
=2l^2\left|\begin{array}{ccccccc}
\cos\theta & + & \cos^2\theta & + & \ldots & & \cos^{N-1}\theta \\
 & + & \cos\theta & + & \ldots & & \cos^{N-2}\theta \\
 & & & + & \ldots & \ldots & \ldots \\
 & & & & + & \ldots & \cos^2\theta \\
 & & & & & + & \cos\theta
\end{array}\right|
=2l^2\cos\theta\left|\begin{array}{c}
\dfrac{1-\cos^{N-1}\theta}{1-\cos\theta} \\
+\ldots \\
+\dfrac{1-\cos\theta}{1-\cos\theta}
\end{array}\right|
$$

$$
=2l^2\frac{\cos\theta}{1-\cos\theta}\left(N-1-\cos\theta\frac{1-\cos^{N-1}\theta}{1-\cos\theta}\right)
$$

$$
\left\langle h^2\right\rangle=\frac{Nl^2(1-\cos\theta)}{1-\cos\theta}+\frac{2Nl^2\cos\theta}{1-\cos\theta}-\frac{2l^2\cos\theta}{1-\cos\theta}-\frac{2l^2\cos^2\theta\left(1-\cos^{N-1}\theta\right)}{(1-\cos\theta)^2}
\longrightarrow
\left\langle h^2\right\rangle_{\text{fr}}=Nl^2\frac{1+\cos\theta}{1-\cos\theta}
$$

$$
\left\langle h^2\right\rangle_{\text{fr}}>\left\langle h^2\right\rangle_{\text{fj}}
$$

理想高分子链$<h^2>$和$<R_g^2>$的关系

对于自由连接链和自由旋转链

$$\left\langle R_g^2 \right\rangle = \left\langle \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(\boldsymbol{r}_i - \boldsymbol{r}_j \right)^2 \right\rangle / N^2$$

$$\left\langle R_g^2 \right\rangle = \frac{\left\langle h^2 \right\rangle}{6}$$

理想链的$<R_g^2>$

$$\sum_{i=1}^{n}\sum_{j=i+1}^{n}\boldsymbol{r}_{ij}^2=\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\boldsymbol{r}_{ij}\cdot\boldsymbol{r}_{ij}$$

$$\boldsymbol{r}_{ij}=\boldsymbol{R}_j-\boldsymbol{R}_i$$

$\boldsymbol{r}_{ij}$原子i和j的距离矢量

$\boldsymbol{S}_i$原子i和质心的距离矢量

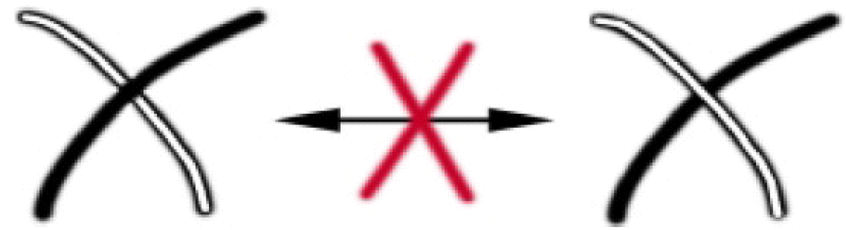
$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\boldsymbol{r}_{ij}\cdot\boldsymbol{r}_{ij}=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\boldsymbol{R}_j-\boldsymbol{R}_i\right)\cdot\left(\boldsymbol{R}_j-\boldsymbol{R}_i\right)=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\boldsymbol{R}_i^2+\boldsymbol{R}_j^2-2\boldsymbol{R}_i\cdot\boldsymbol{R}_j\right)$$

$$\sum_{i=1}^{N}\boldsymbol{R}_i^2=NR_g^2\qquad\sum_{i=1}^{N}\sum_{j=1}^{N}\boldsymbol{R}_i^2=N^2R_g^2\qquad\left\langle-\sum_{i=0}^{n}\sum_{j=0}^{n}\boldsymbol{R}_i\cdot\boldsymbol{R}_j\right\rangle=-\left\langle\sum_{i=0}^{n}\boldsymbol{R}_i\cdot\sum_{j=0}^{n}\boldsymbol{R}_j\right\rangle=0$$

$$\left\langle R_g^2\right\rangle=\left\langle\sum_{i=1}^{N}\sum_{j=i+1}^{N}\boldsymbol{r}_{ij}^2\right\rangle/N^2=\left\langle\sum_{i=1}^{N}\sum_{j=i+1}^{N}\left(\boldsymbol{r}_i-\boldsymbol{r}_j\right)^2\right\rangle/N^2$$

理想高分子链模型几何统计理论结果的适用性

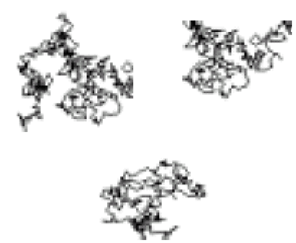
Topological restrictions



体积排除

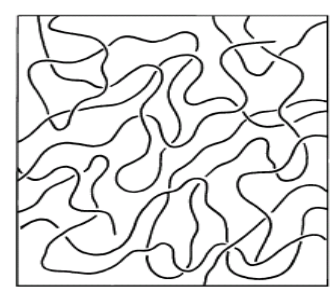
1.模型的局限性

稀溶液反而有问题



矛盾??

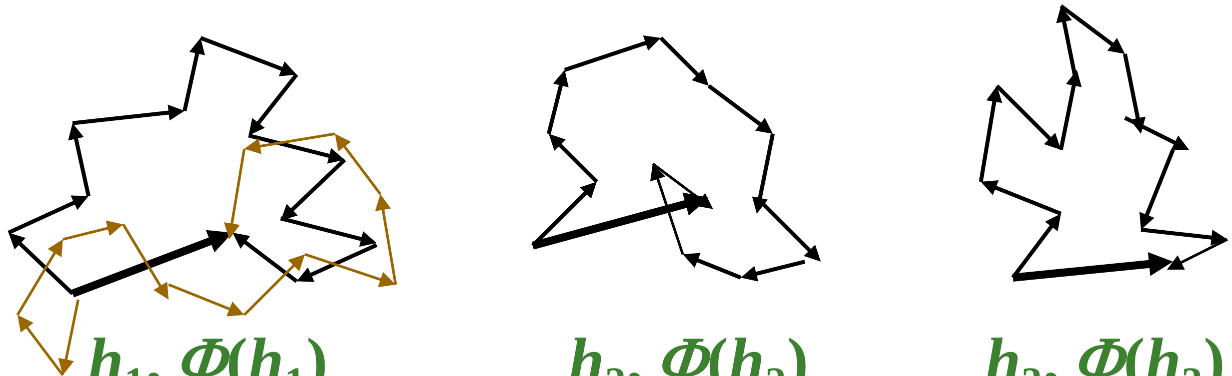
适合Θ溶液,熔体



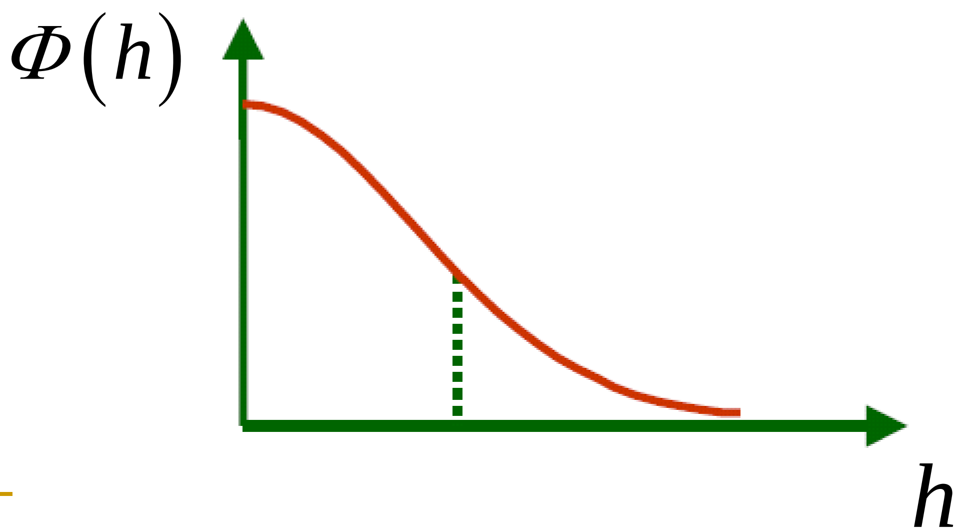
2. 几何统计方法的局限性

不知道具体的概率分布

2.2.4.2 理想高分子链模型的概率统计方法



$h_1, \Phi(h_1)$ $h_2, \Phi(h_2)$ $h_3, \Phi(h_3)$ …

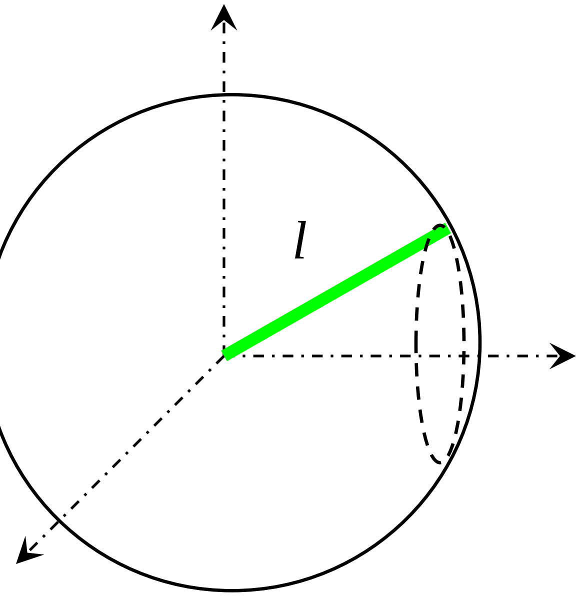


$$\langle h^2 \rangle = \int h^2 \Phi(h)\, dh$$

$$\langle R_g^2 \rangle = \int R_g^2 \Phi(h)\, dh$$

单键的概率分布函数$\psi(\boldsymbol{h}_i)$

- 对于单个键矢量的概率分布函数



$$\psi\left(\boldsymbol{h}_i\right)=\frac{1}{4\pi l^2}\delta\left(\left|\boldsymbol{h}_i\right|-l\right)$$

$$\int \mathrm{d}\boldsymbol{h}_i\psi\left(\boldsymbol{h}_i\right)=1$$

球壳 & 快速旋转单键的散射函数

$$\int \mathrm{d}\boldsymbol{h} \exp\left(-i\boldsymbol{k}\cdot\boldsymbol{h}\right)\psi\left(\boldsymbol{h}\right)$$

$$=\frac{1}{4\pi l^2}\int_0^\infty \mathrm{d}h h^2 \delta\left(h-l\right)\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta \sin\theta \exp\left(-ikh\cos\theta\right)$$

$$=\frac{1}{4\pi l^2}\int_0^\infty \mathrm{d}h h^2 \delta\left(h-l\right)\int_0^{2\pi}\mathrm{d}\phi\int_{-1}^{1}\mathrm{d}x \exp\left(ikhx\right)$$

$$=\frac{1}{2l^2}\int_0^\infty \mathrm{d}h h^2 \delta\left(h-l\right)\frac{1}{ikh}\left[e^{ikh}-e^{-ikh}\right]$$

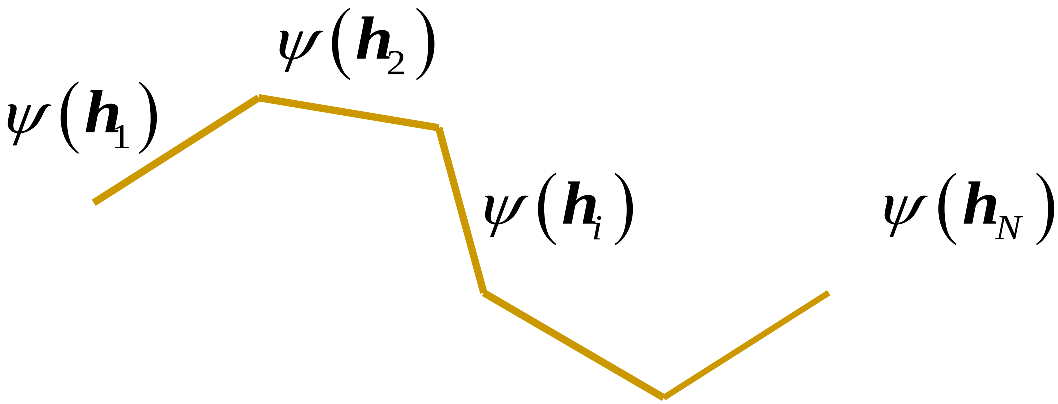
$$=\frac{1}{2l^2}\int_0^\infty \mathrm{d}h h^2 \delta\left(h-l\right)\frac{2}{kh}\sin kh$$

$$=\frac{1}{2l^2} l^2 \frac{2}{kl}\sin kl$$

$$=\frac{\sin kl}{kl}$$

高分子链的总概率分布函数 $\Psi(\{\boldsymbol{h}_N\})$

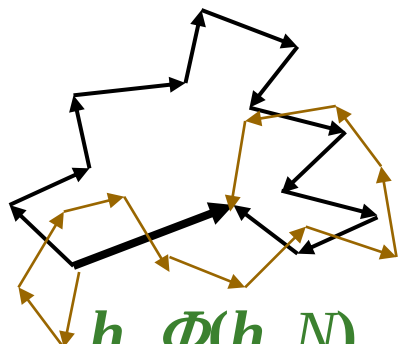
某一构象组态 $\{\boldsymbol{h}_N\}=(\boldsymbol{h}_1 \ldots \boldsymbol{h}_N)$



$$\Psi\left(\{\boldsymbol{h}_N\}\right)=\prod_{i=1}^{N}\psi\left(\boldsymbol{h}_i\right)$$

满足末端距=$\boldsymbol{h}$的自由连接链的概率分布函数 $\Phi(\boldsymbol{h}, N)$

末端矩矢量 $$\boldsymbol{h} = \sum_{i=1}^{N} \boldsymbol{h}_i$$



$\boldsymbol{h}$, $\Phi(\boldsymbol{h}, N)$

$$\Phi(\boldsymbol{h}, N) = \int \mathrm{d}\boldsymbol{h}_1 \int \mathrm{d}\boldsymbol{h}_2 \ldots \int \mathrm{d}\boldsymbol{h}_N \, \delta\left(\boldsymbol{h} - \sum_{i=1}^{N} \boldsymbol{h}_i\right) \Psi\left(\{\boldsymbol{h}_i\}\right)$$

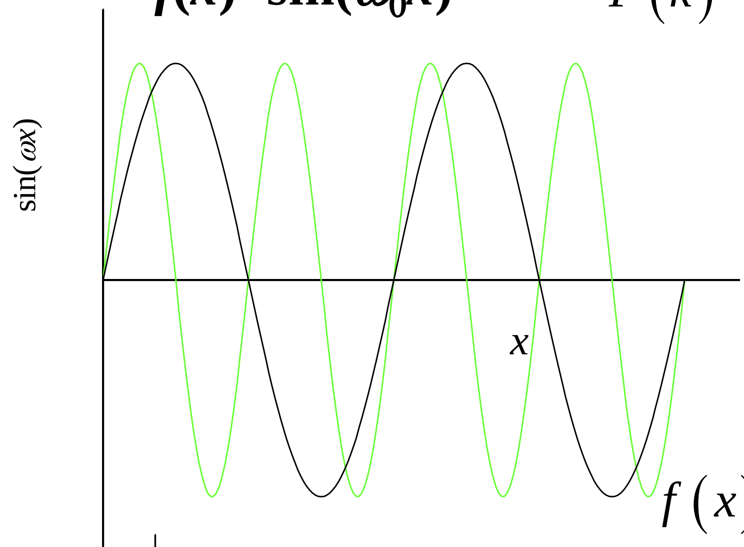
$$\delta(x) = \begin{cases} 1 & x = 0 \\ 0 & x \neq 0 \end{cases} = \frac{1}{(2\pi)^3} \int \mathrm{d}\boldsymbol{k} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

δ函数的Fourier变换原函数

$f(x)=\sin(\omega_0 x)$

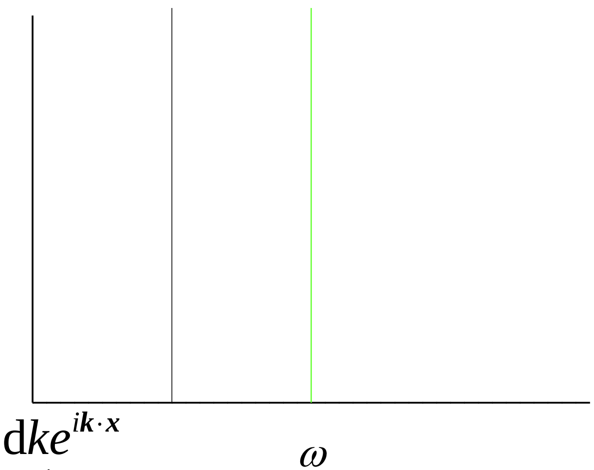
$$F(k)=\frac{1}{(2\pi)^3}\int f(x)\,\mathrm{d}x e^{-ik\cdot x}$$

$F(k=\omega_0)=1$



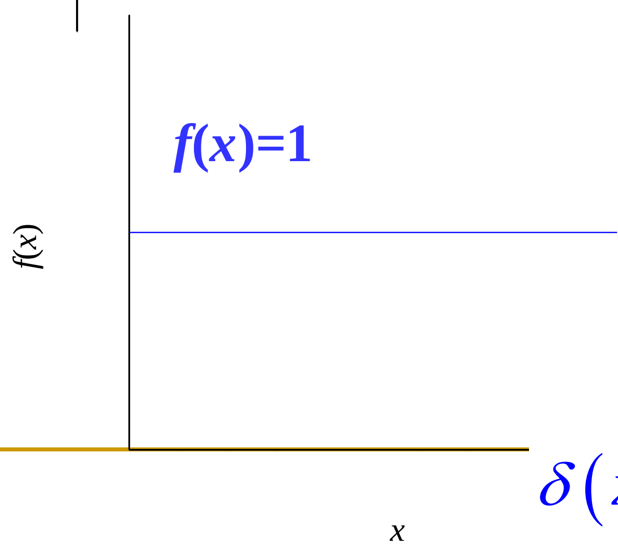
FT

iFT



$$f(x)=\frac{1}{(2\pi)^3}\int F(k)\,\mathrm{d}k e^{ik\cdot x}$$

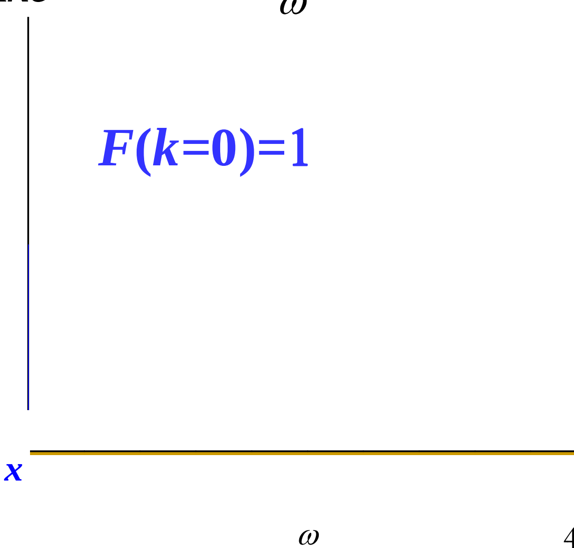
$f(x)=1$



FT

iFT

$F(k=0)=1$



$$\delta(x)=\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k} e^{ik\cdot x}$$

末端距概率分布函数Φ(*h*, *N*)

$$\Phi(\boldsymbol{h},N)=\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}\int \mathrm{d}\boldsymbol{h}_1\int \mathrm{d}\boldsymbol{h}_2\ldots\int \mathrm{d}\boldsymbol{h}_N \exp\left[i\boldsymbol{k}\cdot\left(\boldsymbol{h}-\sum_{i=1}^{N}\boldsymbol{h}_i\right)\right]\Psi(\{\boldsymbol{h}_i\})$$

$$\Psi(\{\boldsymbol{h}_N\})=\prod_{i=1}^{N}\psi(\boldsymbol{h}_i)$$

$$=\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}\int \mathrm{d}\boldsymbol{h}_1\ldots\int \mathrm{d}\boldsymbol{h}_N\prod_{i=1}^{N}\exp(-i\boldsymbol{k}\cdot\boldsymbol{h}_i)\psi(\boldsymbol{h}_i)$$

$$=\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}\left[\int \mathrm{d}\boldsymbol{h}\exp(-i\boldsymbol{k}\cdot\boldsymbol{h})\psi(\boldsymbol{h})\right]^N$$

$$\psi(\boldsymbol{h}_i)=\frac{1}{4\pi l^2}\delta(|\boldsymbol{h}_i|-l)$$

$$\int \mathrm{d}\boldsymbol{h}\exp(-i\boldsymbol{k}\cdot\boldsymbol{h})\psi(\boldsymbol{h})=\frac{\sin(kl)}{kl}$$

末端距概率分布函数Φ(*h*, *N*)

$$\Phi(\boldsymbol{h},N)=\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}\left(\frac{\sin kl}{kl}\right)^N$$

$$\approx\frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}e^{i\boldsymbol{k}\cdot\boldsymbol{h}}\exp\left(-\frac{Nk^2l^2}{6}\right)$$

$$=\frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\left[\int_{-\infty}^{\infty}\mathrm{d}k_\alpha\exp\left(ik_\alpha h_\alpha-Nk_\alpha^2l^2/6\right)\right]$$

$$=\frac{1}{(2\pi)^3}\prod_{\alpha=x,y,z}\left(\frac{6\pi}{Nl^2}\right)^{1/2}\exp\left(-\frac{3}{2Nl^2}h_\alpha^2\right)$$

$$=\left(\frac{3}{2\pi Nl^2}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{h}^2}{2Nl^2}\right)$$

$$\left(\frac{\sin kl}{kl}\right)^N\approx\left(1-\frac{k^2l^2}{6}\right)^N\approx\exp\left(-\frac{Nk^2l^2}{6}\right)$$

$$\int_{-\infty}^{+\infty}\exp\left(-ax^2+bx\right)dx=\left(\frac{\pi}{a}\right)^{1/2}\exp\left(\frac{b^2}{4a}\right)$$

从自由连接链到高斯链

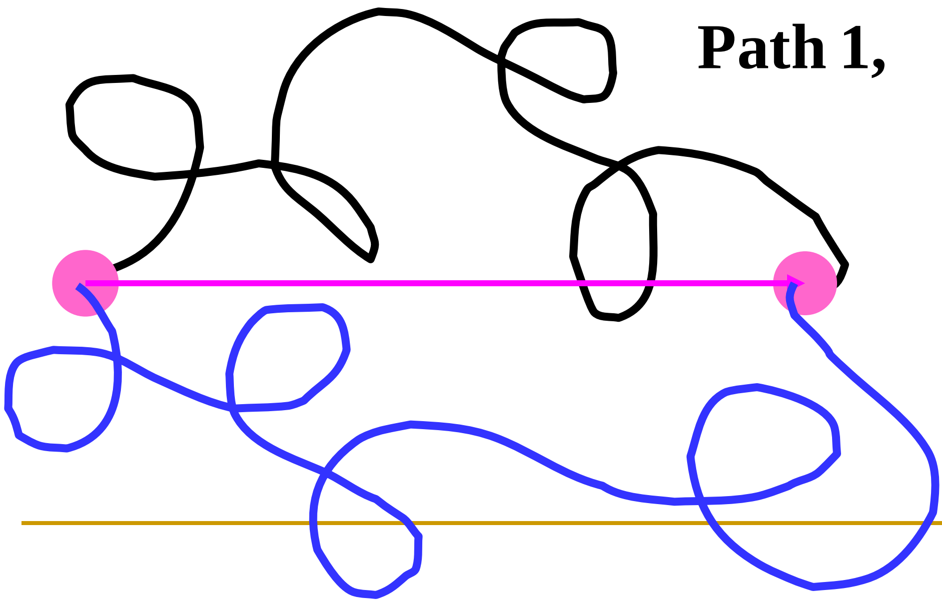
$$N \longrightarrow \infty \qquad \Phi(\boldsymbol{h}, N) \neq 0$$

每个链构象出现的概率是相同的，
只是在每个末端距下概率分布不同。

概率分布函数$\Phi(\boldsymbol{h}, N)$的物理意义

满足末端矩=$\boldsymbol{h}$的自由连接链的概率分布函数$\Phi(\boldsymbol{h}, N)$

= 固定了两端距离及方向、步长和步数,有多少路可走



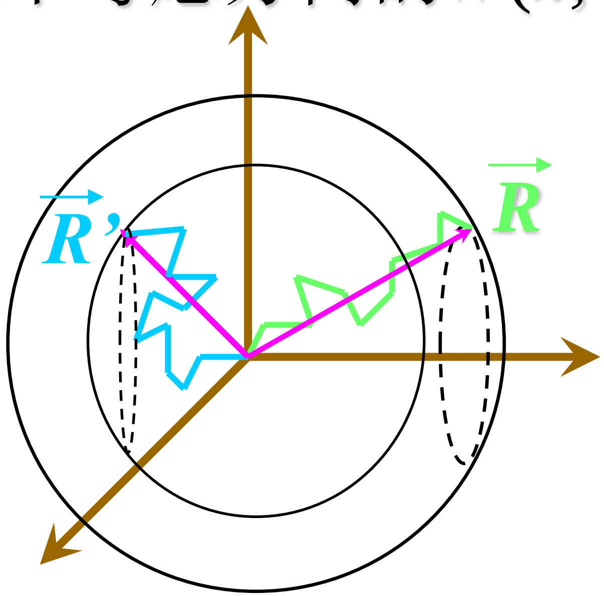
Path 1,

Path 2,

… Path *i*,

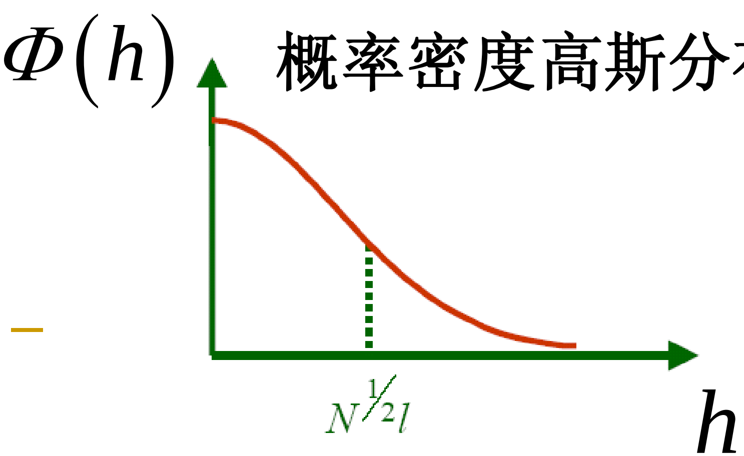
无规行走
(random walk)

只考虑末端距长度不考虑方向的$W(h, N)$

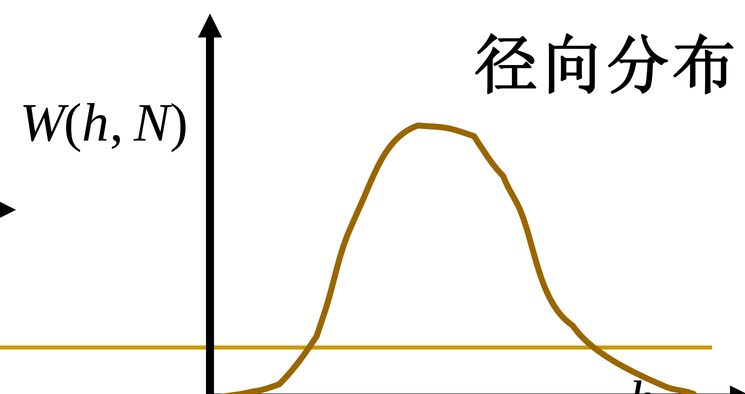


$$\Phi(\vec{R}, N) \longrightarrow W(h,N)=\left(\frac{3}{2\pi N l^2}\right)^{3/2}\exp\left(-\frac{3h^2}{2Nl^2}\right)4\pi h^2$$

概率密度高斯分布



径向分布



末端距分布函数Φ(*h*, *N*)的应用

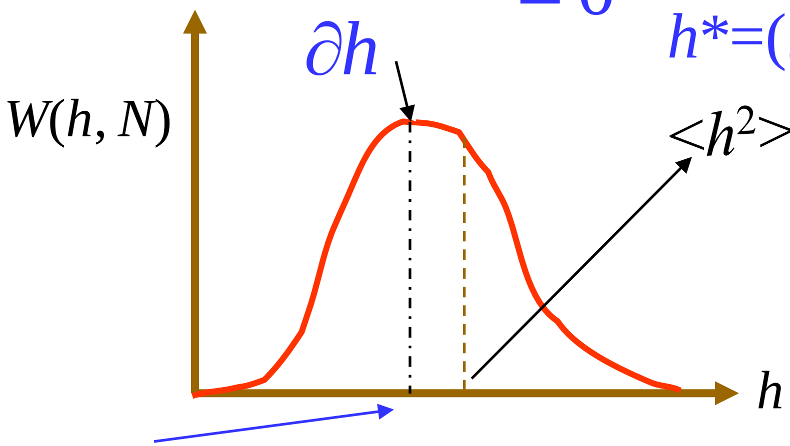
$$\langle h^2 \rangle=\int_0^\infty h^2\left(\frac{3}{2\pi Nl^2}\right)^{3/2}\exp\left(-\frac{3h^2}{2Nl^2}\right)4\pi h^2\mathrm{d}h = Nl^2$$

$$\frac{\partial W(h,N)}{\partial h}=0$$

$$\langle h\rangle = \frac{2}{\sqrt{\pi}}\left(\frac{2N}{3}\right)^{1/2} l$$

$h^*=(2N/3)^{1/2}\, l$

$\langle h^2\rangle^{1/2}=N^{1/2} l$



$$\int_0^\infty e^{-ax^2}x^{2m}\mathrm{d}x=\frac{(2m-1)!!}{2^{m+1}a^m}\sqrt{\frac{\pi}{a}}$$

$$\int_0^\infty x^p e^{-ax}\mathrm{d}x=\frac{p!}{a^{p+1}}$$

理想高分子链-Ideal Polymer Chain

无规飞行链

Random walk

末端距满足高斯分布 $\longrightarrow$

无限长的自由连接链

$$\langle R_{\mathrm{RW}}^2 \rangle \sim N^1$$

高斯链Gaussian Chain

或理想链Ideal Chain

真实高分子链-Real Polymer Chain

Excluded volume effect-自避行走链(self-avoiding walk)

$$\langle R_{\mathrm{SAW}}^2 \rangle \sim N^{6/5}$$

1. 不同程度的刚性,旋转不自由

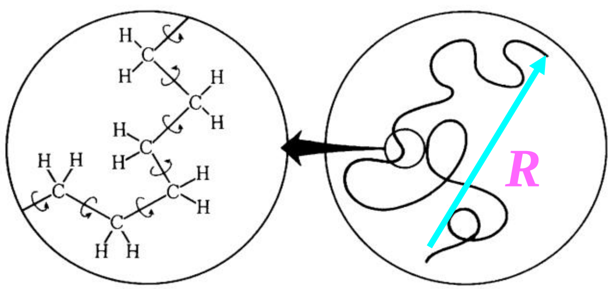
2. 链节-链节有相互作用,链节-溶剂分子有相互作用

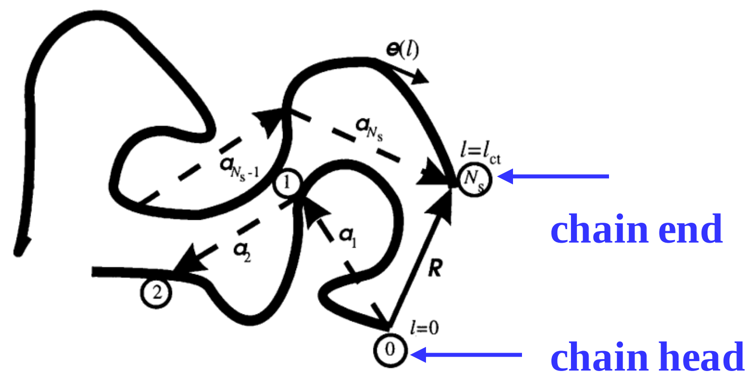
➢ When does the freely jointed chain works－等效自由连接链 & Kuhn segment l_e

(1) 调节溶剂–链节的作用屏蔽掉体积排除效应和链节–链节相互作用 ⟶ 达到Θ温度的溶液, 测得无扰尺寸$\langle h^2\rangle_0 \sim N$

(2) 降低高分子链的分辨率-消除局部的刚性和旋转的不自由

将链重新划分成有效链节数N_e和有效链节长度l_e (Kuhn segment)





"Coarse-grained" (粗粒化) picture:

$$N_e l_e^2 = \langle h^2 \rangle_0$$

$$N_e l_e = L_{max}$$

$$\langle h^2 \rangle_0 = l_e L_{max}$$

L_{max}链的轮廓长度(Contour Length)

例子：PE的N_e和l_e

例子：PE的*Ne*和*le*

实验测得PE： $A = \left(\dfrac{\overline{h}_0^2}{M} \right)^{1/2} = 0.107\text{nm}$

***n*: 聚合度**

N*: 键数=2*n

$$\overline{h}_0^2 = \left[0.107\times10^{-9}\right]^2 \times M = \left[0.107\times10^{-9}\right]^2 \times n \times 28$$

$$= \left[0.107\times10^{-9}\right]^2 \times N/2 \times 28 = 6.76Nl^2$$

$$N_e l_e^2 = \left\langle h^2 \right\rangle_0$$

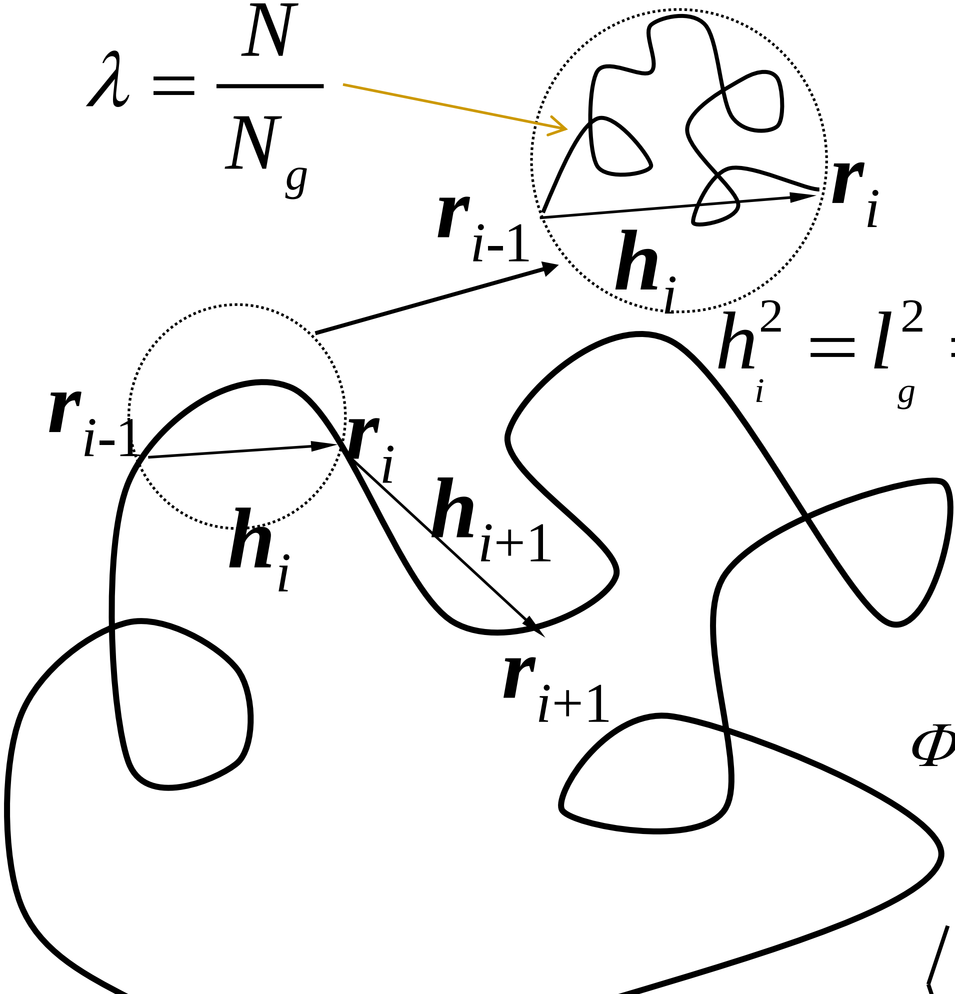
$$N_e l_e = L_{\max}$$

$$l_e = \overline{h}_0^2 / L_{\max} = \frac{6.76Nl^2}{(2/3)^{1/2} Nl} = 8.28l$$

$$N_e = \frac{6.76Nl^2}{(8.28l)^2} = \frac{N}{10}$$

高斯链段与高斯链

$$\lambda = \frac{N}{N_g}$$



$$h_i^2 = l_g^2 = \lambda l^2$$

$$\tilde{\Phi}(\boldsymbol{h}_i, \lambda) = \left(\frac{3}{2\pi\lambda l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}_i^2}{2\lambda l^2}\right)$$

$$\Psi(\boldsymbol{h}, N_g) = \left(\frac{3}{2\pi\lambda l^2}\right)^{3/2} \prod_{i=1}^{N_g} \exp\left(-\frac{3\boldsymbol{h}_i^2}{2\lambda l^2}\right)$$

$$\Phi(\boldsymbol{h}, N_g) = \left(\frac{1}{2\pi N_g l_g^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l_g^2}\right)$$

$$\langle h^2 \rangle = N_g l_g^2$$

Two Definitions of Segment

(1) Kuhn Segment (Kuhn 有效链段)l_e

使整条链末端呈高斯分布所划分出的最小尺寸单元

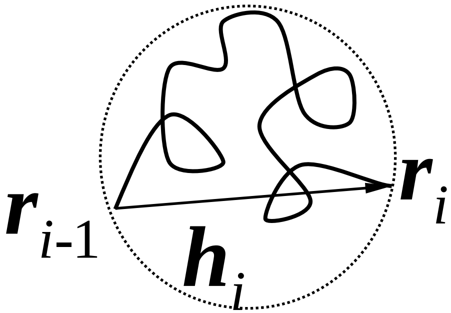
(2) Effective Gaussian Segment (有效高斯链段)l_g

既使整个链末端呈高斯分布, 也要使所划分出的最小尺寸单元末端呈高斯分布

$$l_g > l_e$$

熵簧链

$$\Psi(\boldsymbol{h}, N_g) = \left(\frac{3}{2\pi\lambda l^2}\right)^{3/2} \prod_{i=1}^{N_g} \exp\left(-\frac{3\boldsymbol{h}_i^{\,2}}{2\lambda l^2}\right)$$



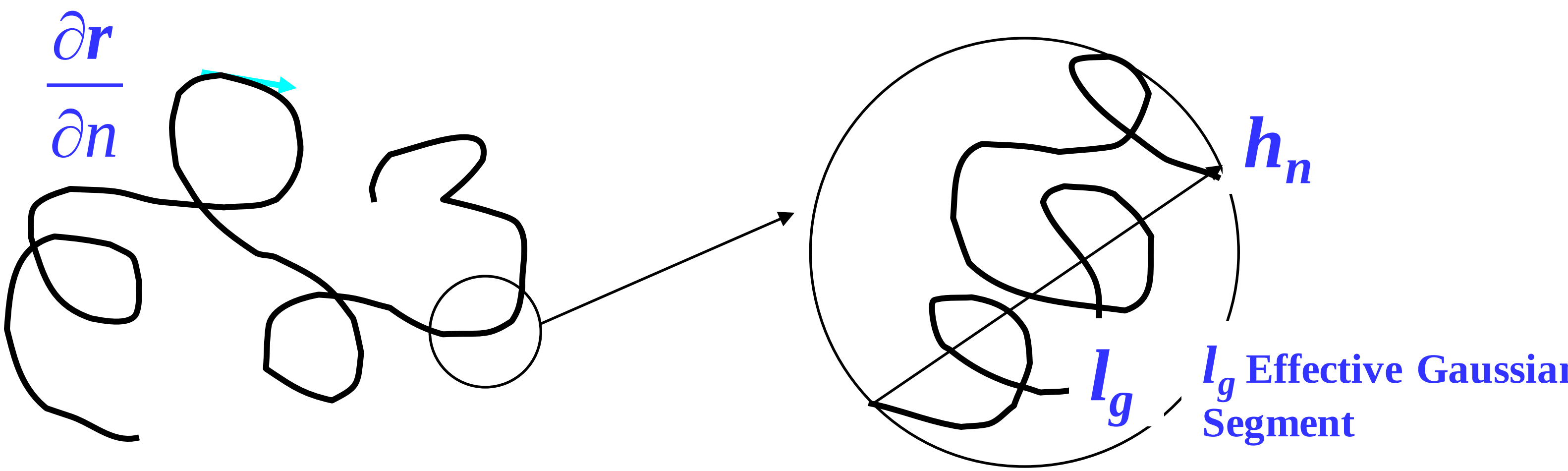
$$u_0(\boldsymbol{r}_i) = \frac{3}{2l_g^2} k_B T \boldsymbol{h}_i^2 = \frac{3}{2l_g^2} k_B T (\boldsymbol{r}_i - \boldsymbol{r}_{i-1})^2$$

$$U_0(\{\boldsymbol{r}_{N_g}\}) = \frac{3}{2l_g^2} k_B T \sum_{i=1}^{N_g} (\boldsymbol{r}_i - \boldsymbol{r}_{i-1})^2$$

$$\Psi(\{\boldsymbol{r}_{N_g}\}) = \left(\frac{3}{2\pi l_g^2}\right)^{3N_g/2} \exp\left(-\frac{U_0(\{\boldsymbol{r}_{N_g}\})}{k_B T}\right)$$

$$= C \exp\left(-\frac{1}{k_B T} \sum_{i=1}^{N_g} u_0(\boldsymbol{r}_i)\right) = C \exp\left(-\frac{1}{k_B T} \int_0^{N_g} \mathrm{d}n\, u_0(\boldsymbol{r}_n)\right)$$

高斯链的连续化描述



由小高斯链组成的高斯长链 $\tilde{\Phi}\left(\boldsymbol{h}_n\right)=\left(\frac{3}{2\pi l_g^{\ 2}}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{h}_n^{\ 2}}{2l_g^{\ 2}}\right)$

$$\Psi\left(\left\{\boldsymbol{h}_n\right\}\right)=\prod_{n=1}^{N_g}\tilde{\Phi}=\prod_{n=1}^{N_g}\left(\frac{3}{2\pi l_g^{\ 2}}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{h}_n^{\ 2}}{2l_g^{\ 2}}\right)$$

$$=\left(\frac{3}{2\pi l_g^{\ 2}}\right)^{3N_g/2}\exp\left[-\sum_{n=1}^{N_g}\frac{3\left(\boldsymbol{r}_n-\boldsymbol{r}_{n-1}\right)^2}{2\left(n-\left(n-1\right)\right)^2 l_g^{\ 2}}\right]$$

$$\frac{\boldsymbol{r}_n-\boldsymbol{r}_{n-1}}{n-\left(n-1\right)}\rightarrow\frac{\partial \boldsymbol{r}}{\partial n}$$

$$\sum_{n=1}^{N_g}\rightarrow\int_0^{N_g}\mathrm{d}n$$

$$=C\cdot\exp\left(-\frac{3}{2l_g^{\ 2}}\int_0^{N_g}\left(\frac{\partial \boldsymbol{r}}{\partial n}\right)^2\mathrm{d}n\right)$$

$$L = nl_g \qquad \Delta s = \Delta n l_g$$

$$\Psi = C\exp\left[-\sum_{n=1}^{N_\mathrm{g}} \frac{3\left(\boldsymbol{r}_n - \boldsymbol{r}_{n-1}\right)^2}{2\Delta n l_\mathrm{g}{}^2}\right] = C\exp\left(-\sum_{n=1}^{N_g} \frac{3\left(\boldsymbol{r}_n - \boldsymbol{r}_{n-\Delta n}\right)^2}{2 l_g \Delta s}\right)$$

$$\lim_{\Delta s \to 0} \sum_{n=1}^{N_g} \left[\frac{\boldsymbol{r}(s_n) - \boldsymbol{r}(s_n - \Delta s)}{\Delta s}\right]^2 \Delta s = \lim_{\Delta s \to 0} \sum_{i=1}^{N_g} \left[\frac{\partial \boldsymbol{r}(s)}{\partial s}\right]^2 \Delta s = \int_0^L \left[\frac{\partial \boldsymbol{r}(s)}{\partial s}\right]^2 \mathrm{d}s$$

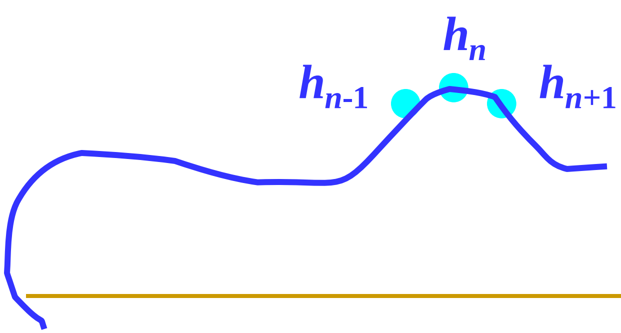
$$\Psi = C\exp\left(-\frac{3}{2l_g}\int_0^L \left[\frac{\partial \boldsymbol{r}(s)}{\partial s}\right]^2 \mathrm{d}s\right)$$

考虑外场和链刚性的链模型

完全柔性链 $$\Psi(\boldsymbol{h})_{flexible} = C \cdot \exp\left(-\frac{3}{2l_{\mathrm{g}}} \int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s} \right)^2 \mathrm{d}s - \frac{1}{k_B T} \int_0^L U_e(s) \mathrm{d}s \right)$$

半刚性蠕虫状链 $$\Psi(\boldsymbol{h})_{sf} = C \cdot \exp\left(-\frac{3}{2l_{\mathrm{g}}} \int_0^L \left(\frac{\partial \boldsymbol{r}}{\partial s} \right)^2 \mathrm{d}s - \frac{\kappa}{2k_B T} \int_0^L \left(\frac{\partial^2 \boldsymbol{r}}{\partial s^2} \right) \mathrm{d}s \right)$$

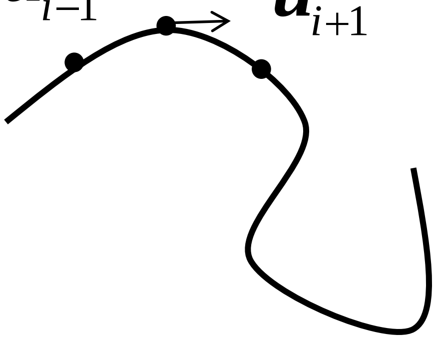
Semi-flexible worm-like chain



κ链弯曲弹性能系数

Bending Energy of Worm-like Chain

$$\Psi\left(\{\boldsymbol{h}_n\}\right) \propto \exp\left(-\frac{3}{2l}\int_0^L \left(\frac{\partial \boldsymbol{r}(s)}{\partial s}\right)^2 \mathrm{d}s - 1/k_B T \sum_{n=1}^{N} U_{\text{bend}}(\boldsymbol{r}_n) \right)$$



$\hat{\boldsymbol{u}}_i = \boldsymbol{r}_i / |\boldsymbol{r}_i|$ 第i个链段取向方向的单位矢量

$$U_{\text{bend}}(\boldsymbol{r}_i) = -\kappa_0 \hat{\boldsymbol{u}}_i \cdot \hat{\boldsymbol{u}}_{i+1} = \frac{\kappa_0}{2}\left|\hat{\boldsymbol{u}}_{i+1} - \hat{\boldsymbol{u}}_i\right|^2 + \text{const.}$$

κ_0是弯曲弹性系数, $\kappa = \kappa_0 l$

$$U_{\text{bend}}\left[\boldsymbol{h}(s)\right] = \frac{\kappa_0 \Delta s^2}{2}\left|\frac{\hat{\boldsymbol{u}}(s+\Delta s) - \hat{\boldsymbol{u}}(s)}{\Delta s}\right|^2 = \frac{\kappa_0 \Delta s^2}{2}\left|\frac{\Delta\left(\partial \boldsymbol{r}(s)/\partial s\right)}{\Delta s}\right|^2 \approx \lim_{\Delta s \to 0}\frac{\kappa_0 \Delta s^2}{2}\left|\frac{\partial\left(\partial \boldsymbol{r}(s)/\partial s\right)}{\partial s}\right|^2$$

$$= \frac{\kappa_0 \Delta s^2}{2}\left|\frac{\partial^2 \boldsymbol{r}(s)}{\partial s^2}\right|^2$$

高斯链的其他描述方式-扩散方程描述

外场下的柔性链

$$\frac{\partial \Phi(\boldsymbol{r}, N_e)}{\partial N} = \left[\frac{b^2}{6}\frac{\partial^2}{\partial \boldsymbol{r}^2} - \frac{1}{kT}U_e(\boldsymbol{r})\right]\Phi(\boldsymbol{r}, N_e)$$

当$U_e(\boldsymbol{R})=0$时

$$\Phi(\boldsymbol{r}, N_e) = \left(\frac{3}{2\pi N_e l_{\mathrm{g}}^{\,2}}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{r}^2}{2N_e l_{\mathrm{g}}^{\,2}}\right)$$

高斯链模型的重要性

高分子链的合理理论抽象-忽略具体的结构细节

高分子物理的重要基石

- 橡胶弹性理论
- **Flory**溶液理论
- **Rouse-Zimm**链动力学理论
- 凝胶相变理论
- 嵌段共聚物的形态预测

2.2.5 真实高分子链的柔顺性表征

(1) 无扰尺寸*A*—Θ溶液中测得的数据与分子量比

$$A=\left(\left\langle h^2\right\rangle_0/M\right)^{1/2}$$

(2)极限特征比C_∞—与自由连接链相比

$$C_\infty=\left\langle h^2\right\rangle_0/\left\langle h^2\right\rangle_{\mathrm{fj}}=\left\langle h^2\right\rangle_0/Nl^2$$

(3)空间位阻参数σ—与自由旋转链相比

$$\sigma=\left[\left\langle h^2\right\rangle_0/\left\langle h^2\right\rangle_{\mathrm{fr}}\right]^{1/2}=\left[\left\langle h^2\right\rangle_0/Nl^2\frac{1+\cos\theta}{1-\cos\theta}\right]^{1/2}$$

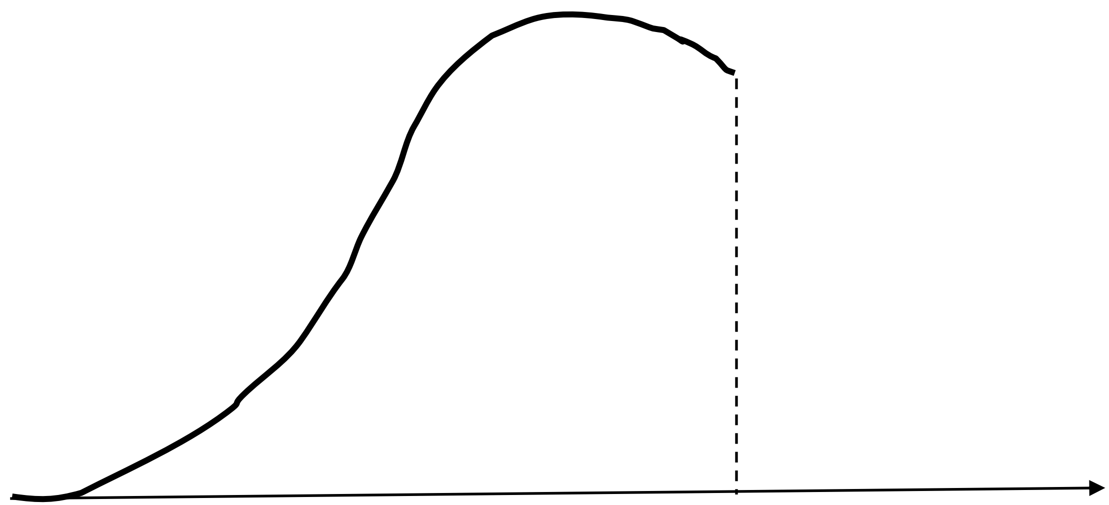
(4) 有效链段长度l_e—与轮廓长度相比

$$l_{\mathrm{e}}=\left\langle h^2\right\rangle_0/L_{\max}$$

(5) 持久长度*a* (persistence length)

无限长的自由旋转链在第一个键方向上的投影

$$a=\frac{1}{l}\sum_{i=1}^{\infty}\langle l_1\cdot l_i\rangle=l\sum_{i=1}^{\infty}\cos^i\theta=\frac{1-\cos^n\theta}{1-\cos\theta}l=\frac{l}{1-\cos\theta}$$



2.2.6 高分子链的实验测量-散射函数

2.2.6.1 自由连接链的散射函数

$$g(\boldsymbol{k})=\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle\frac{\sin|\boldsymbol{k}||\boldsymbol{r}_i-\boldsymbol{r}_j|}{|\boldsymbol{k}||\boldsymbol{r}_i-\boldsymbol{r}_j|}\right\rangle$$

$$g(\boldsymbol{k})=\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle 1-\frac{\boldsymbol{k}^2}{6}(\boldsymbol{r}_i-\boldsymbol{r}_j)^2+\cdots\right\rangle$$

$$\left\langle\sum_{i=1}^{N}\sum_{j=i+1}^{N}(\boldsymbol{r}_i-\boldsymbol{r}_j)^2\right\rangle=N^2\left\langle R_g^2\right\rangle$$

$$=\frac{1}{N}\left(N\cdot N-\frac{\boldsymbol{k}^2}{6}2\left\langle\sum_{i=1}^{N}\sum_{j=i+1}^{N}(\boldsymbol{r}_i-\boldsymbol{r}_j)^2\right\rangle+\cdots\right)$$

$$g(\boldsymbol{k})=\frac{1}{N}\left(N^2-\frac{\boldsymbol{k}^2}{3}N^2\left\langle R_g^2\right\rangle+\cdots\right)=N\left(1-\frac{\boldsymbol{k}^2}{3}\left\langle R_g^2\right\rangle+\cdots\right)$$

2.2.6.2 高斯链的散射函数

链上任意两点*i*和*j*之间形成的链也是高斯链，其中包含|*i*-*j*|个高斯链段，两点之间的末端距：

$$\left\langle \boldsymbol{r}_i - \boldsymbol{r}_j \right\rangle^2 = |i-j|\overline{l_{\mathrm{g}}^2}$$

$$g(\boldsymbol{k}) = \frac{1}{N}\int_0^N \mathrm{d}i \int_0^N \mathrm{d}j \left\langle 1 - \frac{\boldsymbol{k}^2}{6}\left(\boldsymbol{r}_i - \boldsymbol{r}_j\right)^2 + \cdots \right\rangle$$

$$= \frac{1}{N}\int_0^N \mathrm{d}i \int_0^N \mathrm{d}j \left[1 - \frac{\boldsymbol{k}^2}{6}|i-j|\overline{l_{\mathrm{g}}^2} \right]$$

$$= \frac{1}{N}\int_0^N \mathrm{d}i \int_0^N \mathrm{d}j \exp\left[-\frac{\overline{l_{\mathrm{g}}^2}\boldsymbol{k}^2}{6}|i-j| \right]$$

$$= \frac{1}{N}\int_0^N \mathrm{d}i \int_0^N \mathrm{d}j \exp\left[-\boldsymbol{k}^2 \left\langle R_g^2 \right\rangle_g |i-j| \right]$$

Debye 函数

$$g(\boldsymbol{k}) = \frac{1}{N} N^2 f_D\left(\boldsymbol{k}^2 N \langle R_g^2 \rangle_g\right) = N f_D\left(\boldsymbol{k}^2 \langle R_g^2 \rangle\right)$$

Debye 函数 $$f_D(x) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right)$$

(1) $\boldsymbol{k}^2 \langle R_g^2 \rangle << 1$

$$f_D(x) = \frac{2}{x^2}\left(1 - x + x^2/2! - x^3/3! - 1 + x\right) = \left(1 - x/3\right)$$

$$g(\boldsymbol{k}) = N\left(1 - \frac{\boldsymbol{k}^2}{3}\langle R_g^2 \rangle + \cdots\right)$$

Ornstein-Zernike 近似

(2) $\boldsymbol{k}^2 \left\langle R_g^2 \right\rangle > 1$

$$f_D(x) = \frac{2}{x^2}\left(e^{-x} - 1 + x\right) = \frac{2}{x}$$

$$g(\boldsymbol{k}) = \begin{cases} N\left(1 - \boldsymbol{k}^2 \left\langle R_g^2 \right\rangle / 3\right) & |\boldsymbol{k}|^2 \left\langle R_g^2 \right\rangle << 1 \\ 2N / \boldsymbol{k}^2 \left\langle R_g^2 \right\rangle & |\boldsymbol{k}|^2 \left\langle R_g^2 \right\rangle >> 1 \end{cases}$$

Ornstein-Zernike 近似式

$$g(\boldsymbol{k}) = \frac{N}{1 + \boldsymbol{k}^2 \left\langle R_g^2 \right\rangle / 2}$$

附录: Debye函数的由来

$$g(\boldsymbol{k}) = \frac{1}{N}\int_0^N \mathrm{d}i \int_0^N \mathrm{d}j \exp\left[-\boldsymbol{k}^2 \left\langle R_g^2 \right\rangle_g |i-j|\right] \qquad s = j/N, \qquad t = i/N$$

$$Q = k^2 l_g^2 N_g / 6 = k\left\langle R_g^2 \right\rangle$$

$$f_D(Q) = \int_0^1 \left[\int_0^1 \exp\left(-Q|s-t|\right) ds\right] dt$$

$$= \int_0^1 \left[\int_0^t \exp\left[-Q(t-s)\right] ds + \int_t^1 \exp\left[-Q(s-t)\right] ds\right] dt$$

$$= \int_0^1 \left[\exp(-Qt)\int_0^t \exp(Qs)\, ds + \exp(Qt)\int_t^1 \exp(-Qs)\, ds\right] dt$$

$$= \frac{1}{Q}\int_0^1 \left[\exp(-Qt)\left(\exp(Qt)-1\right) - \exp(Qt)\left(\exp(-Q)-\exp(-Qt)\right)\right] dt$$

$$= \frac{1}{Q}\int_0^1 \left[2-\exp(-Qt)-\exp(-Q)\exp(Qt)\right] dt$$

$$= \frac{1}{Q}\left[2+\frac{\exp(-Q)-1}{Q}-\exp(-Q)\frac{\exp(Q)-1}{Q}\right]$$

$$= \frac{1}{Q^2}\left[\exp(-Q)-1+Q\right]$$

无规飞行链
Random walk

无限长的自由连接链

末端距满足高斯分布

$$\left\langle R_{\mathrm{RW}}^2 \right\rangle \sim N^1$$

高斯链Gaussian Chain

或理想链Ideal Chain

真实高分子链-Real Polymer Chain

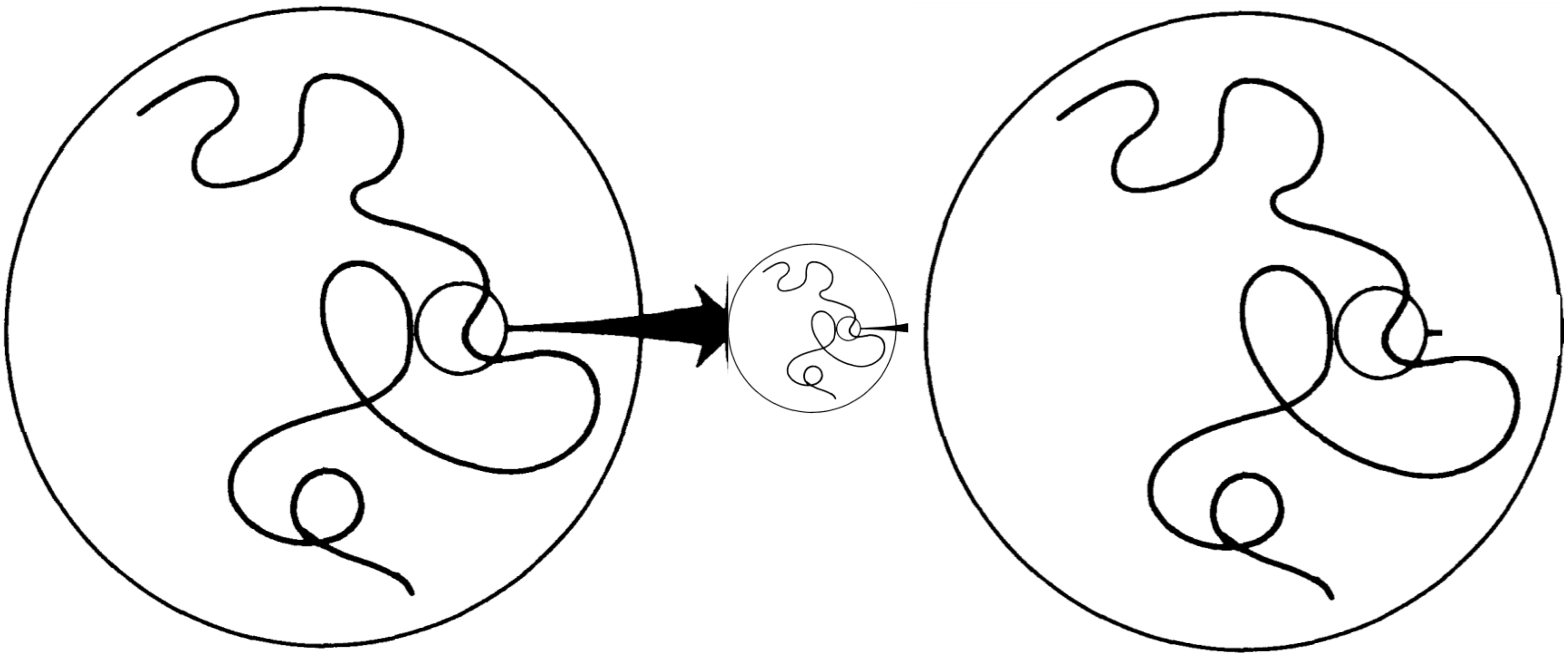
Excluded volume effect-自避行走链(self-avoiding walk)

$$\left\langle R_{\mathrm{SAW}}^2 \right\rangle \sim N^{6/5} \sim N^{2\nu}$$

1. 不同程度的刚性,旋转不自由

2. 链节-链节有相互作用,链节-溶剂分子有相互作用

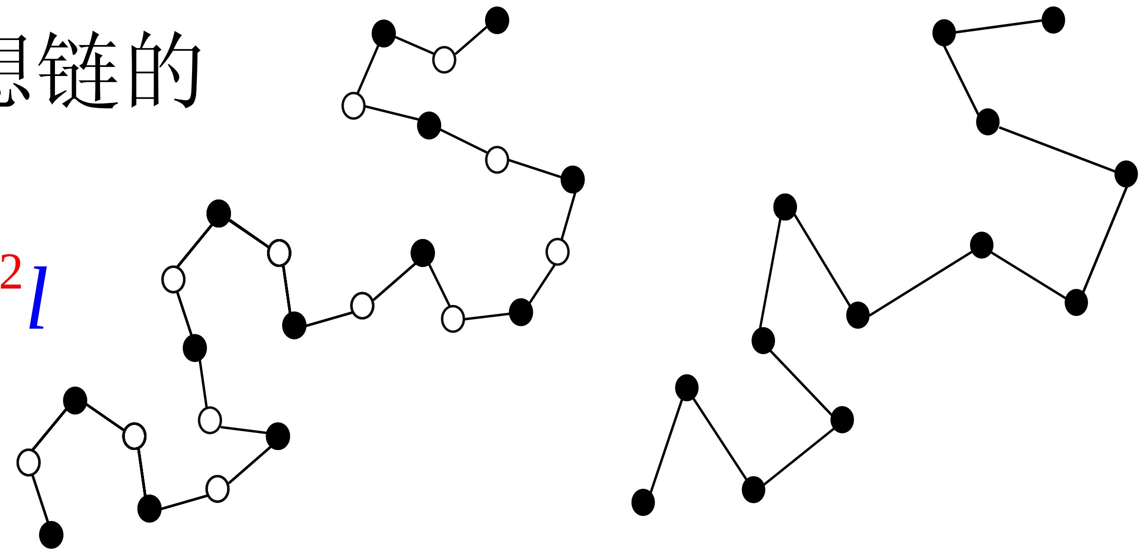
自相似与标度律



2.2.7 标度律- (1) 链的性质

(1a) 理想链的性质

$$h \approx N^{1/2} l$$



$$N \to N/\lambda, \quad l \to l\sqrt{\lambda}$$

$$h = R_g = F(l, N) \qquad F(l, N) = F(\sqrt{\lambda} l, N/\lambda)$$

标度函数：

$$F(l, N) = const. \times \sqrt{\lambda} l \left(N/\lambda\right)^{a=1/2} = const. \times \sqrt{N} l$$

(1b) 真实链的性质 $h \approx N^{\nu} l$

$$N \to N/\lambda, \qquad l \to l\lambda^{\nu}$$

$$h = F\left(l\lambda^{\nu}, N/\lambda\right) = const. \times l\lambda^{\nu}\left(N/\lambda\right)^{a=\nu} = const. \times N^{\nu} l$$

(1c) 高分子链散射函数的标度律

$$g(\mathbf{k}) = F(kl, N) \propto N$$ 无量纲

$$g(\mathbf{k}) \to g(\mathbf{k})/\lambda$$

$$F(kl\lambda^{\nu}, N/\lambda) = \frac{1}{\lambda}F(kl, N)$$

$$g(\mathbf{k}) = F(kl, N) = NF(klN^{\nu}, 1) = NF(kR_g)$$

当k很大时，散射函数仅反映了高分子链内部尺度非常小的散射行为在kR_g>>1时，$g(\mathbf{k})$应与N无关

$$g(\mathbf{k}) = const. \times N(kR_g)^{a=-1/\nu} = const. \times N(klN^{\nu})^{-1/\nu} \propto k^{-1/\nu}$$

$$g(\mathbf{k}) = \begin{cases} N\left(1 - \mathbf{k}^2\left\langle R_g^2\right\rangle/3\right) & |\mathbf{k}|^2\left\langle R_g^2\right\rangle << 1 \\ 2N/\mathbf{k}^2\left\langle R_g^2\right\rangle & |\mathbf{k}|^2\left\langle R_g^2\right\rangle >> 1 \end{cases}$$

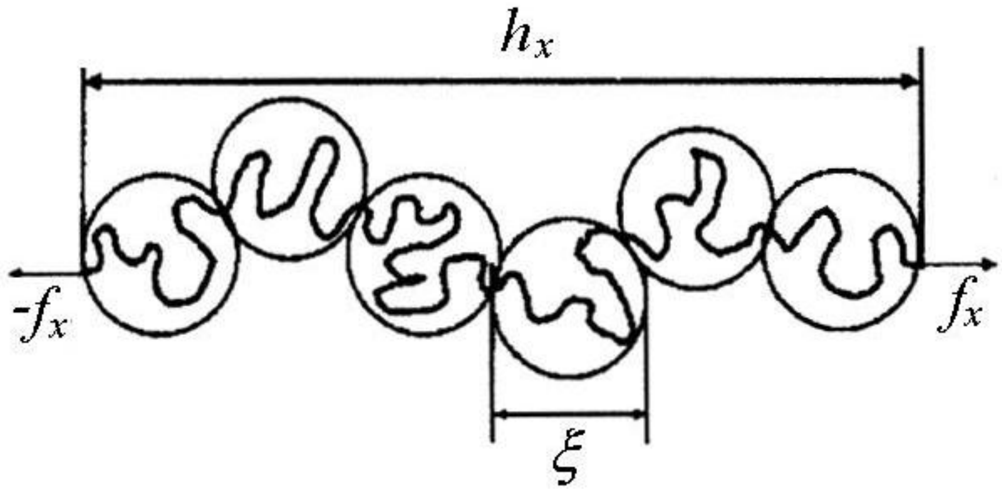
(2) 标度律的另一种形式

$$S = S_0 f(x)$$

$$f(x) = \begin{cases} 1 & x < x^* \\ x^m & x > x^* \end{cases}$$

$$S = S_0 \left(\frac{x}{x^*} \right)^m$$

(3) Blob Model - a. Chain Stretching



$$\xi \sim g^{\nu} l$$

$$g \sim \frac{(Nl)^{1/1-\nu}}{h_x^{1/1-\nu}}$$

$$h_x \sim \xi \frac{N}{g} \sim \frac{Nl^{1/\nu}}{\xi^{1/\nu-1}}$$

$$F \sim k_B T \frac{N}{g} \sim k_B T \left(\frac{h}{N^{\nu} l} \right)^{1/1-\nu}$$

$$f = \frac{\partial F}{\partial h} \sim k_B T \left(\frac{h^{\nu}}{N^{\nu} l} \right)^{1/1-\nu}$$

$$f\big|_{\nu=0.5} \sim k_B T \frac{h}{Nl^2}$$

Stretching of a Gaussian Chain

$$\Phi\left(\boldsymbol{h}, N_g\right) = \left(\frac{1}{2\pi N_g l_g^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l_g^2}\right)$$

$$\Omega\left(\boldsymbol{h}, N_g\right) = \Phi\left(\boldsymbol{h}, N_g\right) \int \Omega\left(\boldsymbol{h}, N_g\right) d\boldsymbol{h} = \left(\frac{3}{2\pi N_g l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l^2}\right) \int \Omega\left(\boldsymbol{h}, N_g\right) d\boldsymbol{h}$$

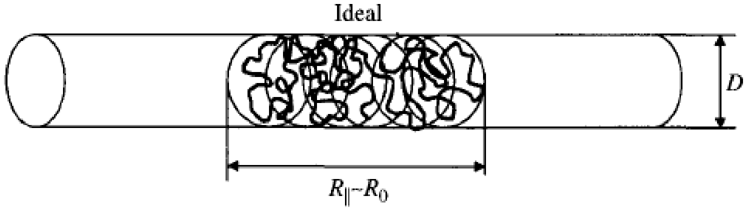
$$S(\boldsymbol{h}, N_g) = -\frac{3}{2} k_B \frac{\boldsymbol{h}^2}{N_g l^2} + \frac{3}{2} k_B \ln\left(\frac{3}{2\pi N_g l^2}\right) + k_B \ln\left[\int \Omega(\boldsymbol{h}, N_g) d\boldsymbol{h}\right]$$

$$F(\boldsymbol{h}, N_g) = U - TS = \frac{3}{2} k_B T \frac{\boldsymbol{h}^2}{N_g l^2} + F(0, N_g)$$

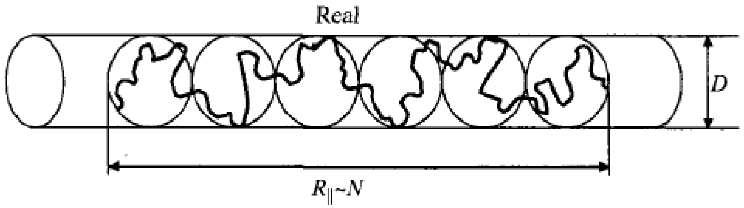
$$\boldsymbol{f} = \frac{\partial F(\boldsymbol{h}, N_g)}{\partial h} = \frac{3k_B T}{N_g l^2} \boldsymbol{h}$$

(3) Blob Model – b. Chain Compression

$$D = g^{\nu} l$$



$$R_{//}\big|_{ideal} \sim \left(\frac{N}{g}\right)^{1/2} D \sim \left(\frac{Nl^2}{D^2}\right)^{1/2} D \approx N^{1/2} l$$



$$R_{//}\big|_{real} \sim \left(\frac{N}{g}\right) D \sim \left(\frac{Nl^{1/\nu}}{D^{1/\nu}}\right) D \sim Nl \left(\frac{l}{D}\right)^{2/3}$$

$$F_{conf}\big|_{ideal} = k_B T \frac{N}{g} = k_B T N \left(\frac{l}{D}\right)^2 = k_B T \left(\frac{h}{D}\right)^2$$

$$F_{conf}\big|_{real} = k_B T \frac{N}{g} = k_B T N \left(\frac{l}{D}\right)^{1/\nu} = k_B T \left(\frac{N^{\nu} l}{D}\right)^{1/\nu} = k_B T \left(\frac{h}{D}\right)^{5/3}$$