2018年第十二届复杂流体流变学培训班

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第一讲：流变现象

第二讲：广义牛顿流体和线性黏弹流体

第三讲：黏弹本构方程

第四讲：微观本构模型

第一讲 流变现象

1.1 流体或固体？

- Deborah数

$$D_e = \frac{\lambda}{1/\dot{\gamma}} = \lambda\dot{\gamma}$$

- $De \ll 1$ →纯粹的牛顿粘性流体
- $De \gg 1$ →纯粹的胡克弹性固体

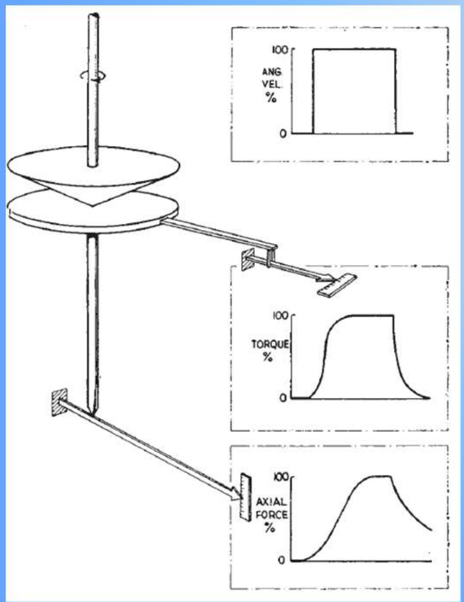
- Weissenberg数

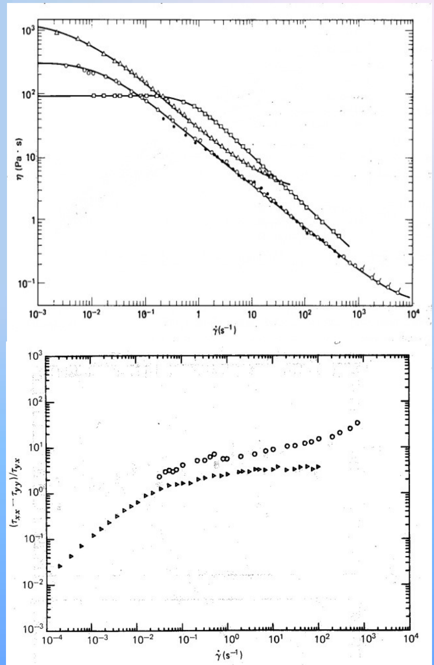
$$W_i = \lambda\dot{\gamma} \quad 或 \quad W_i = \lambda\omega$$

Karl Weissenberg

(11 June 1893 － 6 April 1976)

- 1922-1928发明Weissenberg X射线衍射仪
- 1928-1939提出弹性流体概念和理论模型并给出解析解
- 1946－1952发明Weissenberg 流变仪





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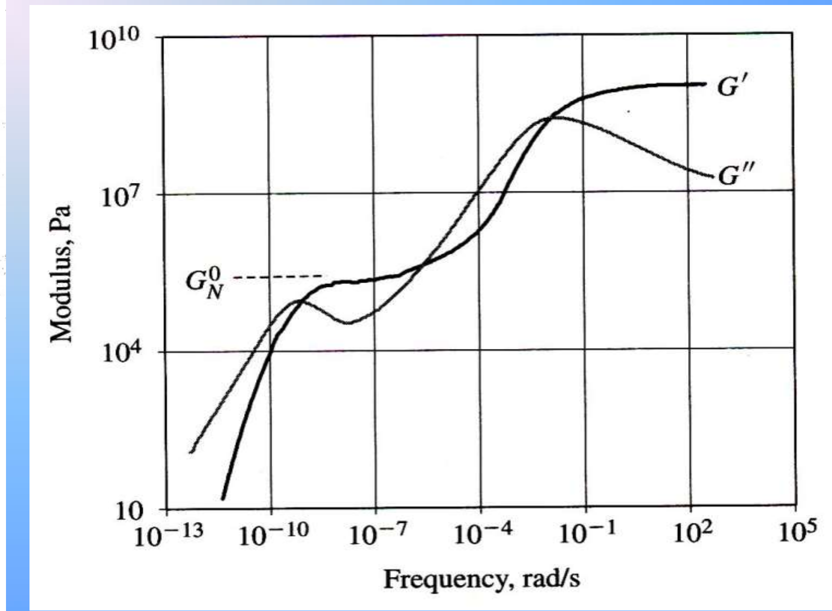
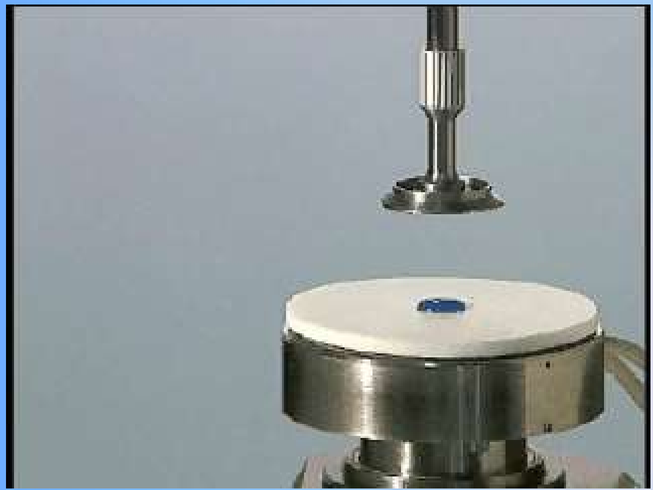
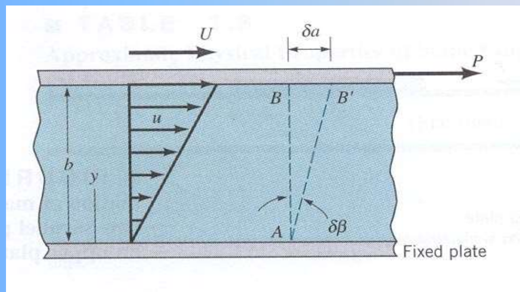


1.2 流变现象

1.2.1 非线性黏度





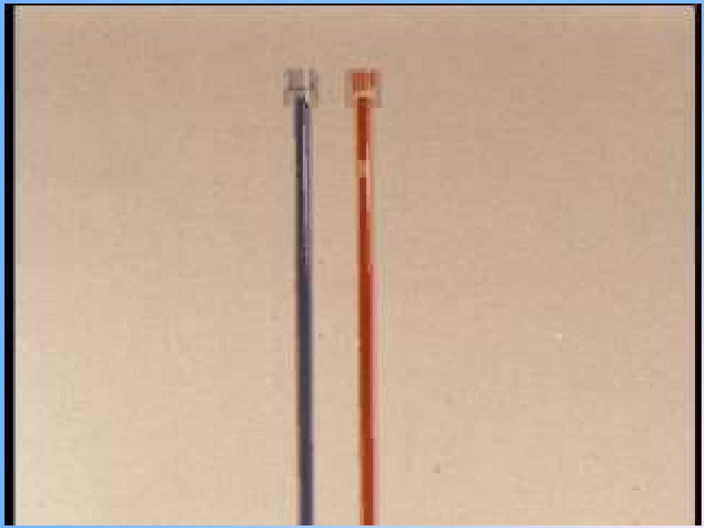
牛顿粘性定律

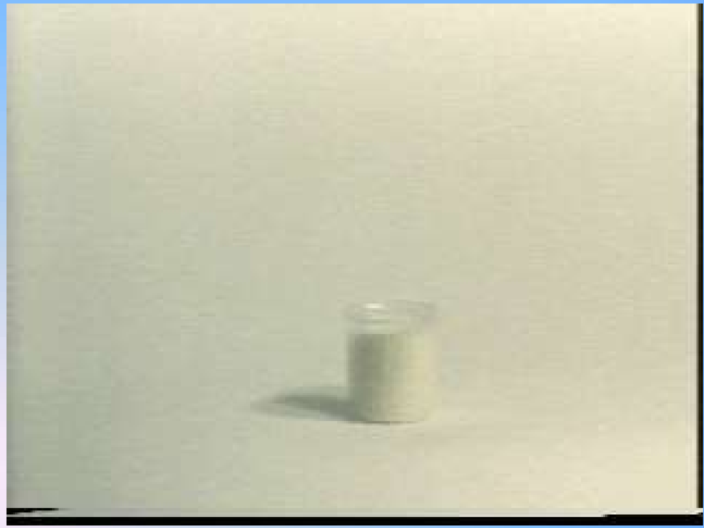
$$\sigma_{xy} = \eta \frac{du}{dy} = \eta \dot{\gamma}$$

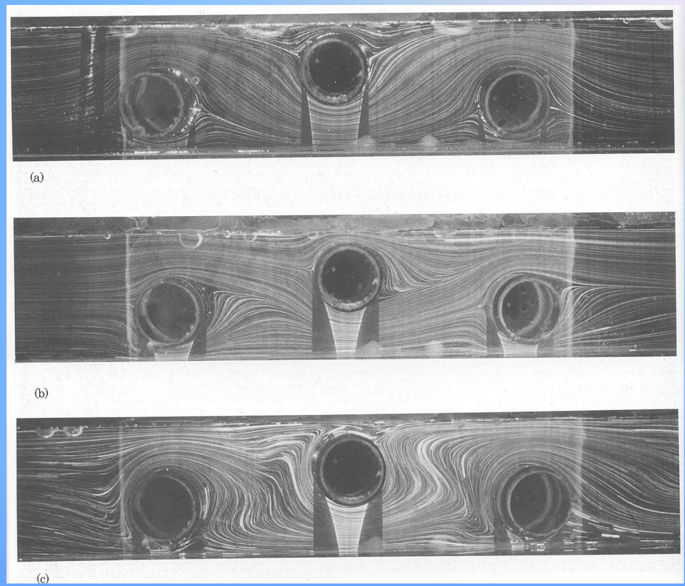
流体	黏度量级 (Pa.s = kg m^{-1} s^{-1})
Glass	10^{40}
Molten glass (500^{o} C)	10^{12}
Bitumen	10^{8}
Polymers	10^{3}
Golden syrup	10^{2}
Liquid honey	10
Glycerol	10^{0}
Olive oil	10^{-1}
Bicycle oil	10^{-2}
Water	10^{-3}
Air	10^{-5}

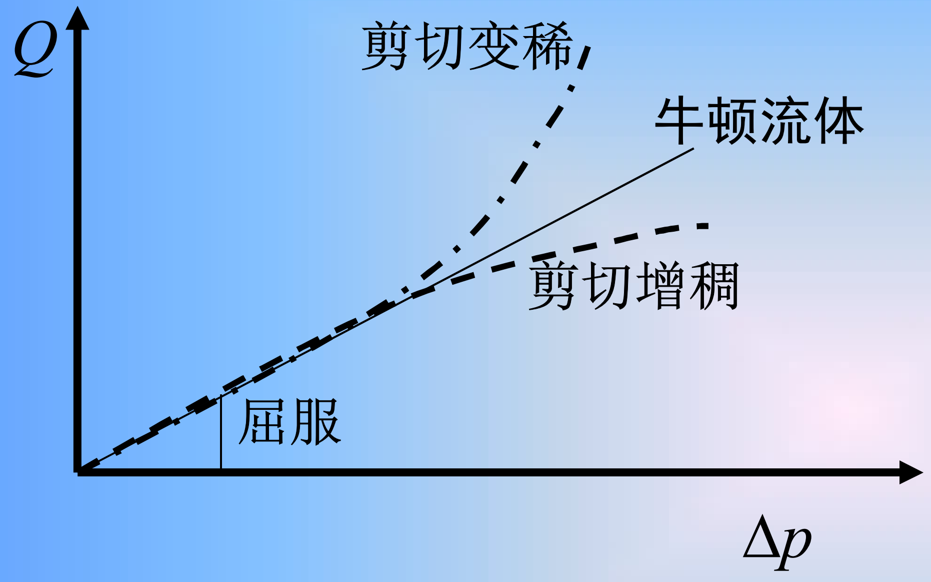
场景	典型应变率（s^{-1}）	应用
Sedimentation of powers	$10^{-6} \sim 10^{-4}$	Medicines, paints
Levelling by surface tension	$10^{-2} \sim 10^{-1}$	Paints, printing inks
Draining under gravity	$10^{-1} \sim 10$	Painting and coating.
Extruders	$1 \sim 10^{2}$	Polymers
Chewing and swallowing	$10 \sim 10^{2}$	Foods
Mixing and stirring	$10 \sim 10^{3}$	Manufacturing liquids
Pipe flow	$10 \sim 10^{3}$	Pumping. Blood flow.
Spraying and brushing	$10^{3} \sim 10^{4}$	Spray-drying, painting
Rubbing	$10^{4} \sim 10^{5}$	Creams/lotion to skins
High speed coating	$10^{5} \sim 10^{6}$	Paper
Lubrication	$10^{3} \sim 10^{7}$	Gasoline engines

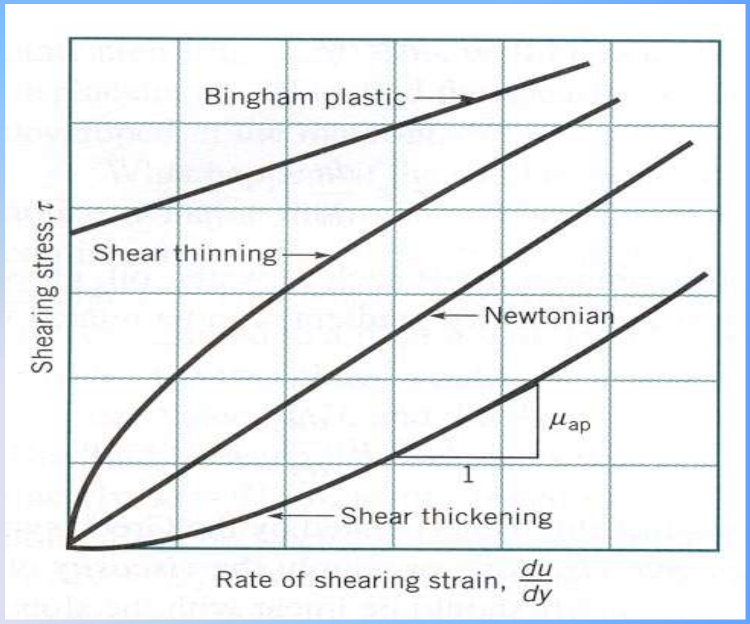
非线性行为 – 流体黏度依赖于应变率







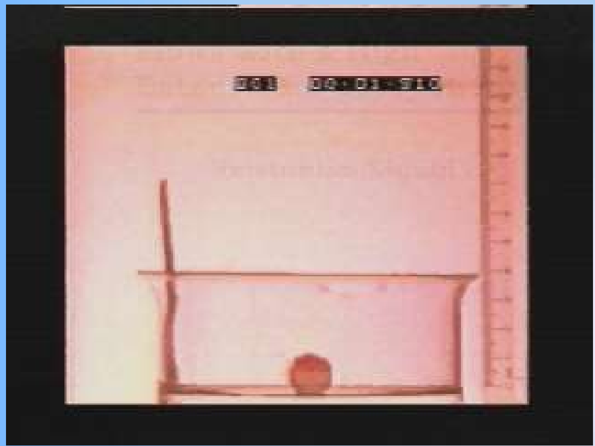
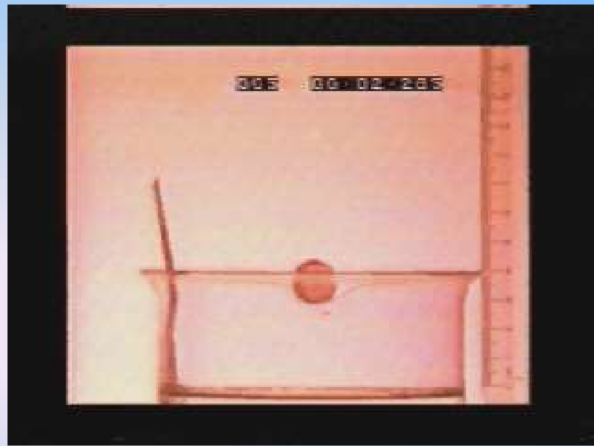


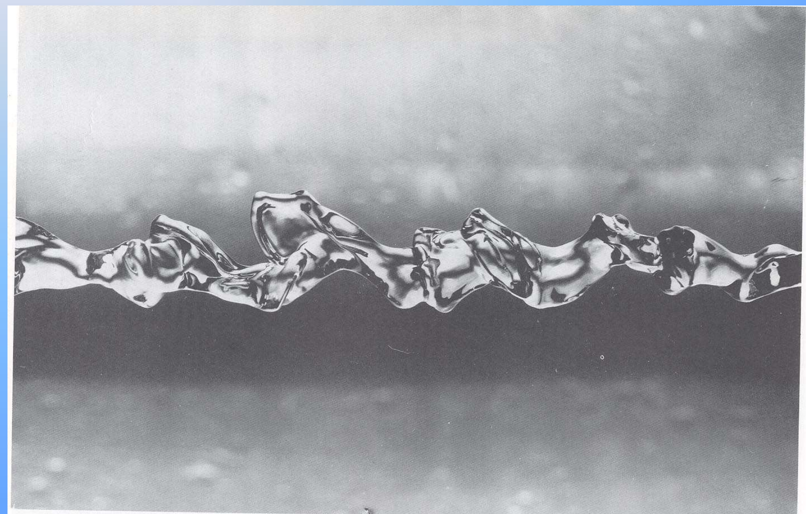


- 剪切变稀 – 黏度随着剪切率的增加而降低（可超万倍）.
- 剪切增稠 – 黏度随着剪切率的增加而增加.
- 屈服应力 – 应力只有超过某个临界值流体才会流动，如番茄酱、牙膏和涂料等。

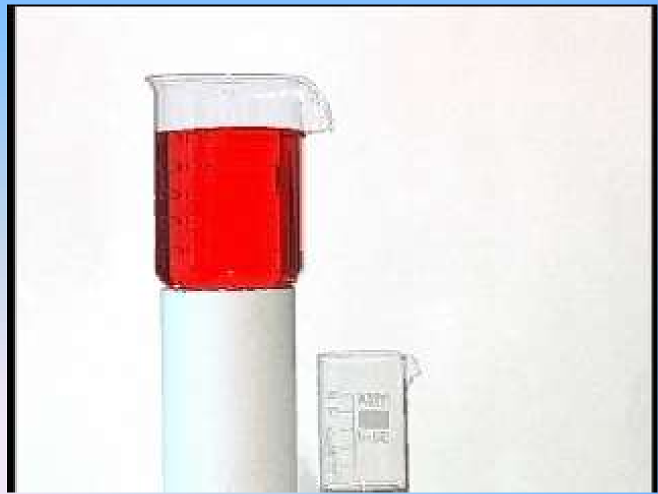
2.2.2 抑制拉伸

- 溅水实验

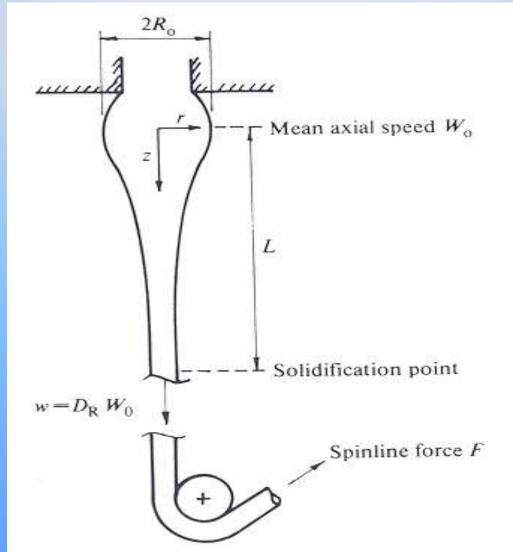





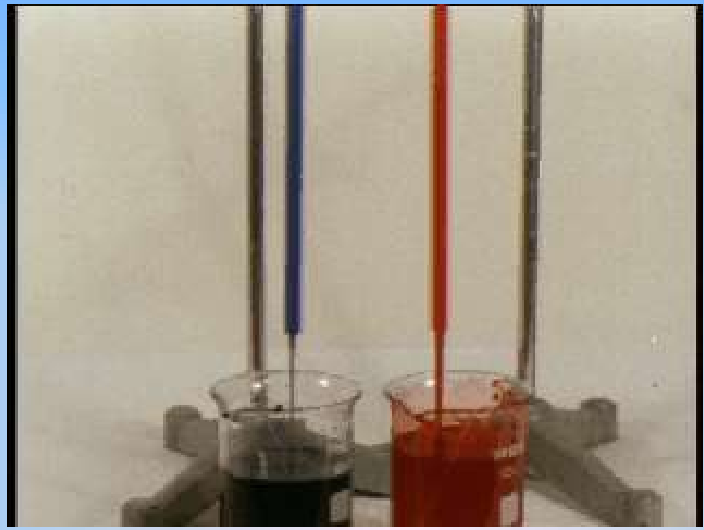
• 开放虹吸效应 ：



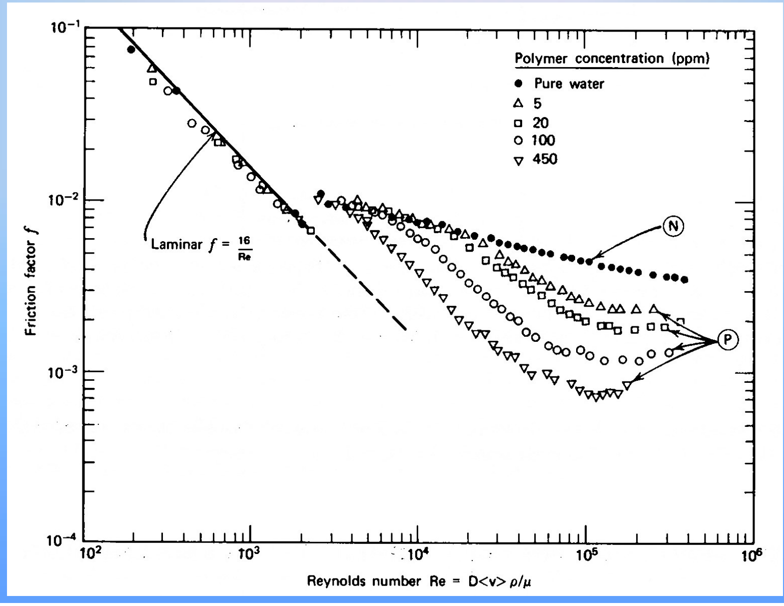
• 纤维纺丝


2R_o
Mean axial speed W_o
r
z
L
Solidification point
$w = D_R W_0$
Spinline force F

- 拉伸粘度对于收缩流动的影响



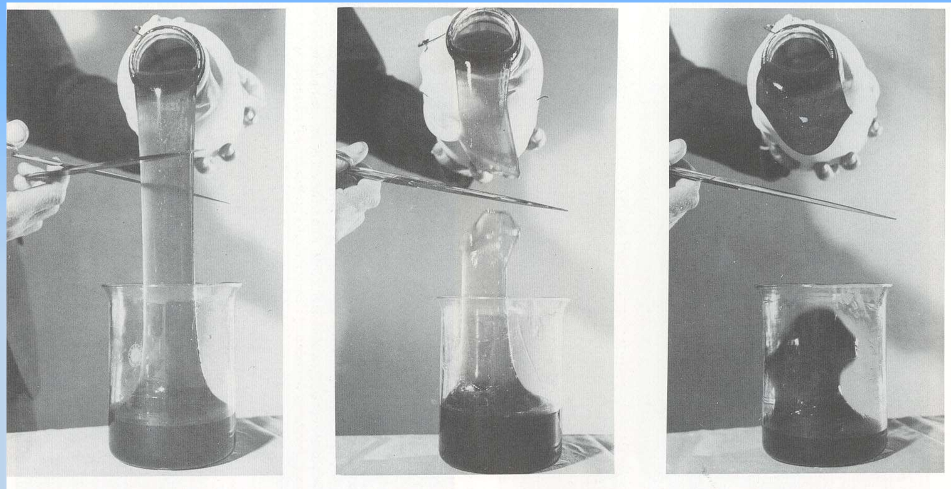
- 湍流减阻



2.2.3.法向应力以及其它弹性效应

- 爬竿或Weissenberg效应：

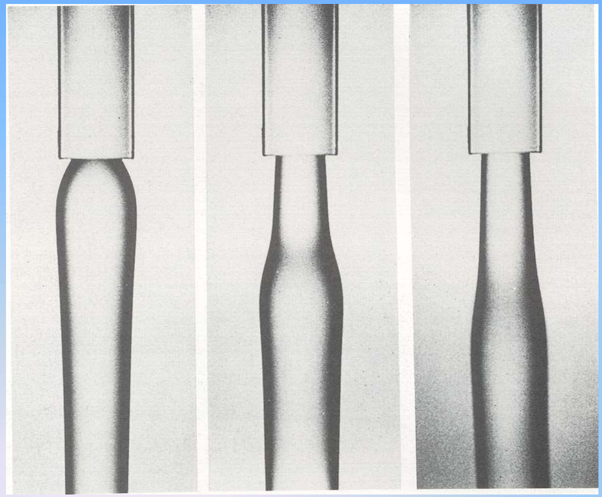
- 弹性回缩



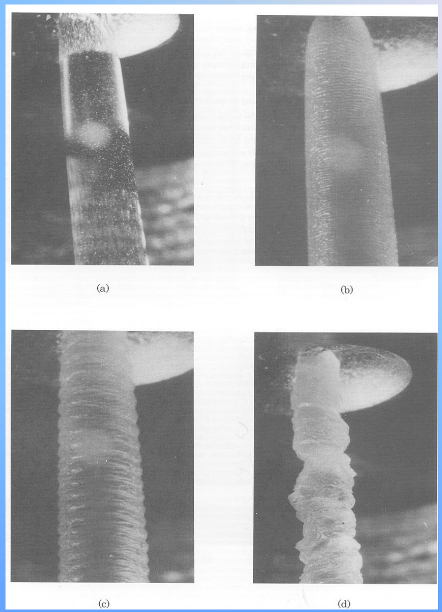
(a) (b) (c)

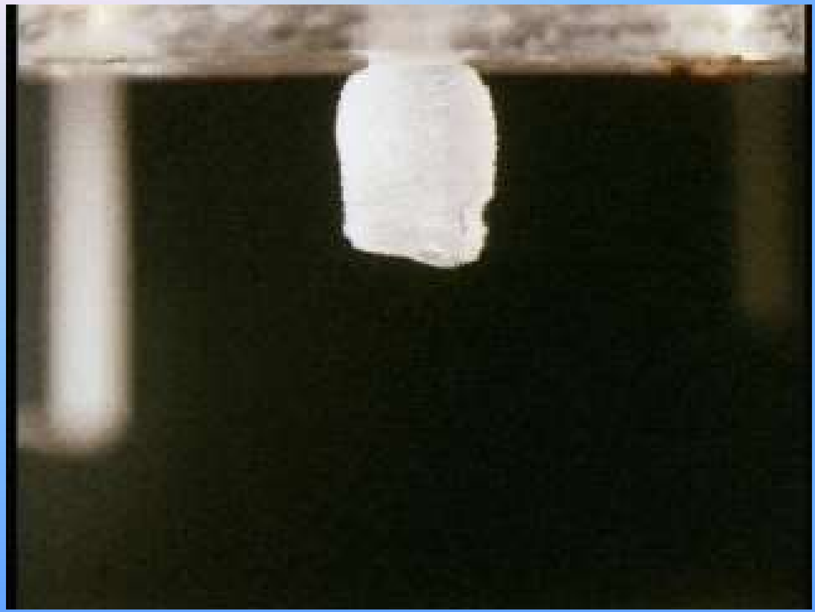
- 挤出膨胀

- 延迟挤出膨胀-

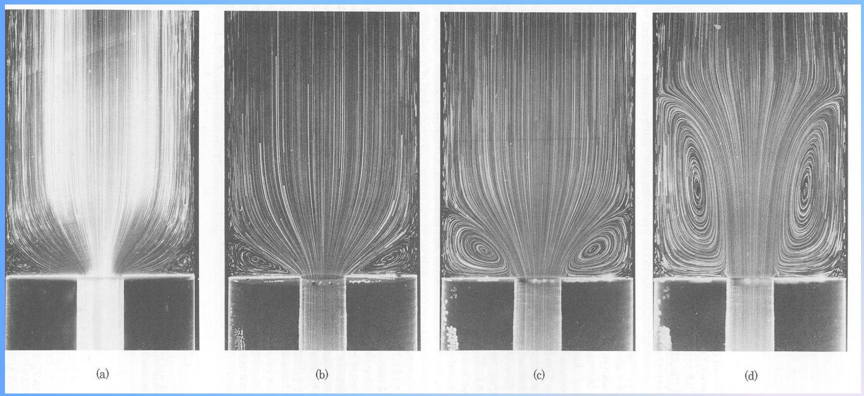


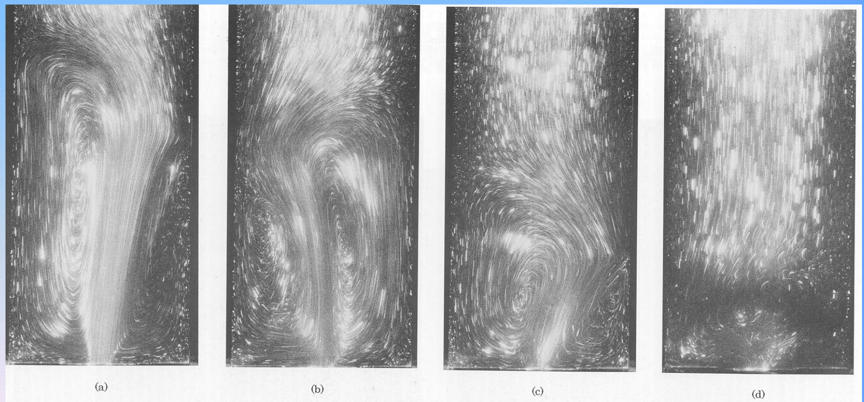
- 从鲨鱼皮状挤出到熔体断裂



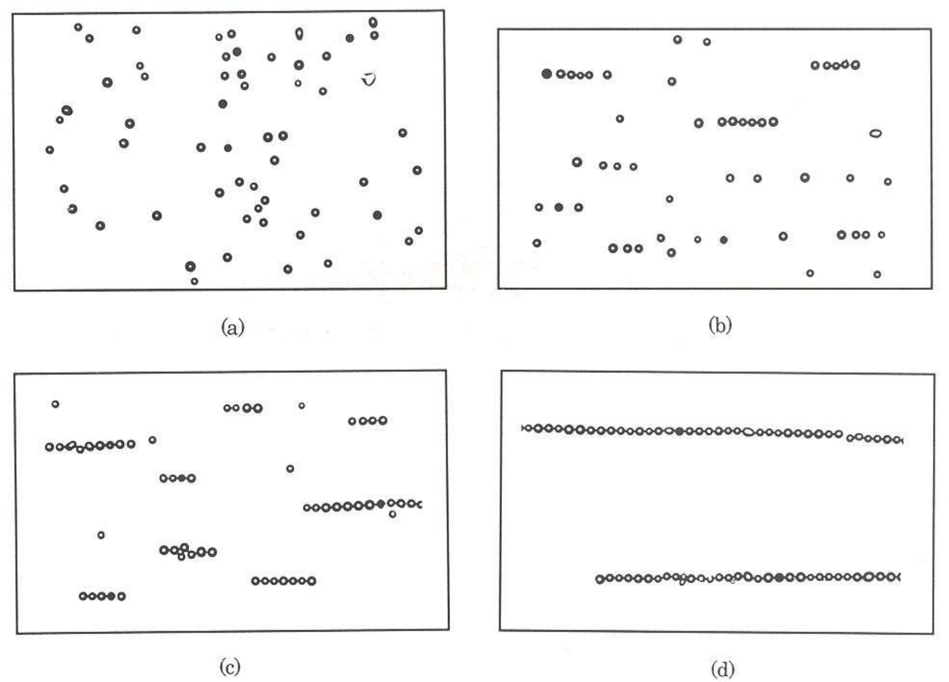


- 流体弹性对突然收缩流动的影响





- 流场下黏弹性流体中悬浮颗粒的（自）排列



- **触变性** – 在恒定剪切速率下表观粘度随时间而降低

- **抗触变性** – 在恒定剪切速率下表观粘度随时间而增加

流变现象小结

- **黏弹性**
- **非线性行为** – 剪切变稀、剪切变稠、屈服应力
- **拉伸黏度** – 抑制拉伸,开放虹吸效应 ，收缩流场下的流动减缓、湍流减阻
- **法向应力** – 爬竿或Weissenberg效应、弹性回缩、挤出膨胀、延迟挤出膨胀、鲨鱼皮状挤出、熔体断裂,突然收缩流动中的涡旋形成 、流场下粘弹性流体中悬浮颗粒的（自）排列
- **触变性与抗触变性** – 黏度对于时间（形变历史）的依赖

第二讲：广义牛顿流体和线性黏弹流体

不可压缩非牛顿流体控制方程，

$$\nabla \cdot \mathbf{v} = 0$$

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla p + \nabla\cdot\boldsymbol{\sigma} + \rho g$$

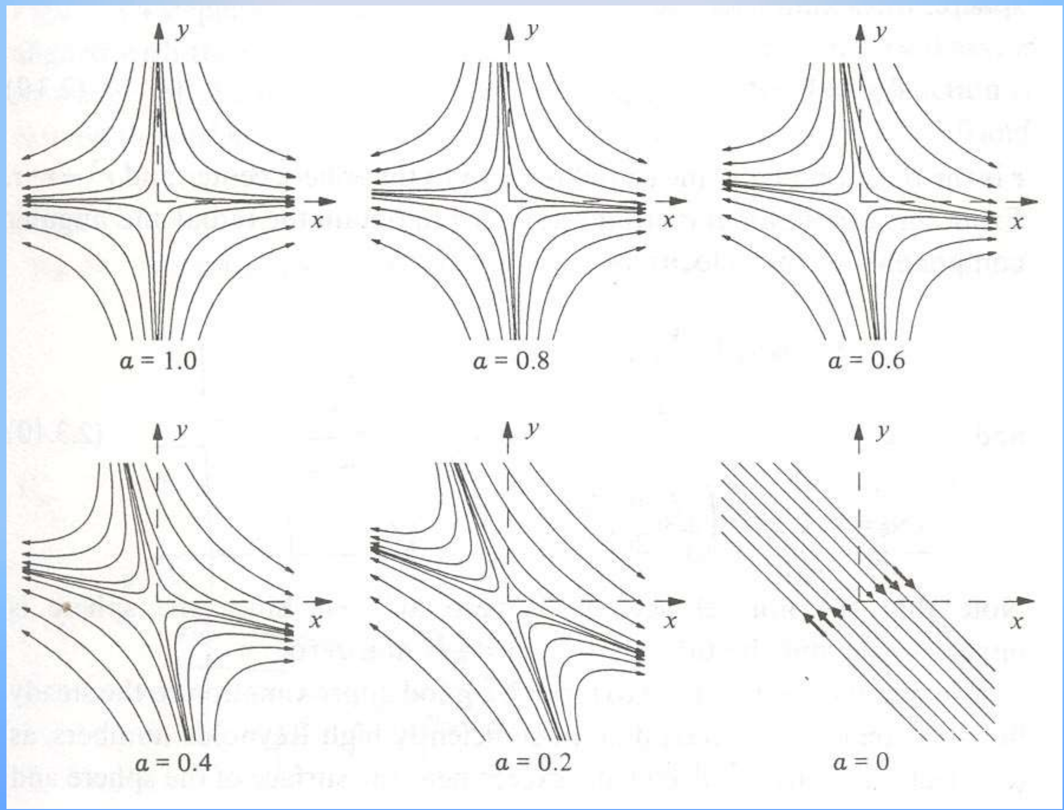
$$\boldsymbol{\sigma} = \eta\left[\nabla\mathbf{v} + \left(\nabla\mathbf{v}\right)^T\right]$$ 应力—应变率本构关系

- 密度（ρ）和黏度（η） 就足以确定牛顿流体的复杂流动.
- 非牛顿流体的本构关系复杂性

$\sigma(t) = \Psi(t,\ \nabla v,\ \nabla r(t)$, 材料特性等).

二维流场下的流体运动学

$$\nabla v = \frac{1}{2}\dot{\gamma}\begin{pmatrix} 1+\alpha & 1-\alpha & 0 \\ -1+\alpha & -(1+\alpha) & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



物质函数

在流变场下的表征：

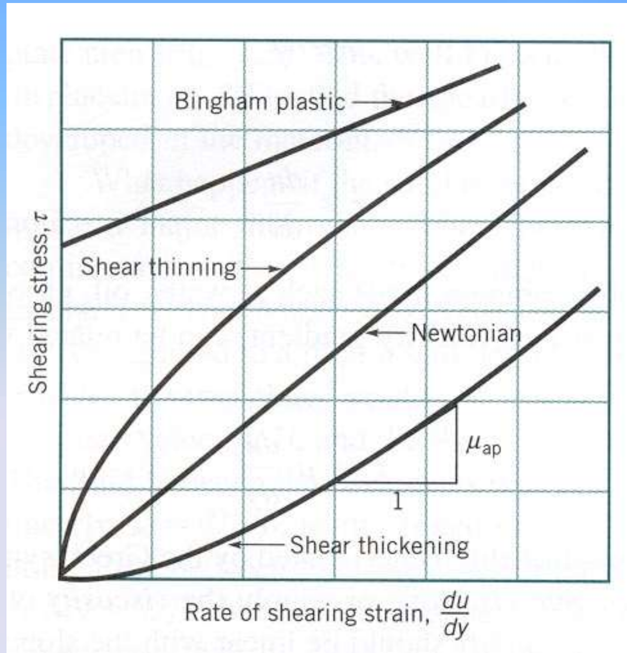
- 选择流动类型，如剪切或拉伸，定常或非定常流动；
- 定义流动参数，如剪切率、拉伸率等；
- 通过应力测量结果计算物质函数。

在流变分析中的作用：

- 为定量评估新材料提供标准测试方法；
- 用于材料的质量控制；
- 为揭示本构关系提供必要的物质信息；
- 针对某特定材料验证本构模型。

2.2 广义牛顿流体本构方程

2.2.1 Bingham 模型



$$\eta(\dot{\gamma}) = \begin{cases} \infty, & \sigma \le \sigma_y \\ \eta_0 + \sigma_y/\dot{\gamma}, & \sigma > \sigma_y \end{cases}$$

σ_y - 屈服应力

η_0 – 高剪切率下的黏度

2.2.2 幂律模型 – $\eta(\dot{\gamma}) = k\left|\dot{\gamma}\right|^{n\text{-}1}$

$$\sigma = \eta\dot{\gamma} = k\left|\dot{\gamma}\right|^n \quad \begin{cases} n < 1, & \text{pseudoplastic or shear thinning} \\ n = 1, & k = \eta, \text{ Newtonian fluids} \\ n > 1, & \text{dilatant or shear thickening} \end{cases}$$

两个经验参数： k (单位: $\mathrm{Pa \cdot s^n}$) 和 n (无量纲)

2.3 从本构关系推导物质函数并求解流动问题

例2.1 利用幂律模型预测稳态单轴拉伸黏度。

解: 单轴拉伸的应变率张量,

$$\dot{\gamma}=\left[\nabla \mathbf{v}+(\nabla \mathbf{v})^{T}\right]=\begin{pmatrix}-\dot{\varepsilon}_0 & 0 & 0\\ 0 & -\dot{\varepsilon}_0 & 0\\ 0 & 0 & 2\dot{\varepsilon}_0\end{pmatrix}$$

其大小为 $|\dot{\gamma}|=\sqrt{\dot{\gamma}:\dot{\gamma}/2}=\dot{\varepsilon}_0\sqrt{3}$

$$\sigma=k|\dot{\gamma}|^{n-1}\left[\nabla \mathbf{v}+(\nabla \mathbf{v})^{T}\right]=\begin{pmatrix}-k\left(3^{\frac{n-1}{2}}\right)\dot{\varepsilon}_0^{n} & 0 & 0\\ 0 & -k\left(3^{\frac{n-1}{2}}\right)\dot{\varepsilon}_0^{n} & 0\\ 0 & 0 & 2k\left(3^{\frac{n-1}{2}}\right)\dot{\varepsilon}_0^{n}\end{pmatrix}$$

$\eta_E(\dot{\varepsilon}_0)\equiv(\sigma_{zz}-\sigma_{xx})/\dot{\varepsilon}_0=3^{\frac{n+1}{2}}k\dot{\varepsilon}_0^{n-1}$ 和 $\eta_E/\eta=\dfrac{3k(\dot{\varepsilon}_0\sqrt{3})^{n-1}}{k(\dot{\varepsilon}_0\sqrt{3})^{n-1}}=3$

例2.2 A Power-Law fluid, $\sigma = \eta\dot{\gamma} = k|\dot{\gamma}|^n$

is located in the space between two parallel plates that are separated by a distance $2h$. The fluid flows under a constant applied pressure gradient $\partial p/\partial x$ according to the equation of motion $\frac{d\sigma}{dy} = \frac{\partial p}{\partial x}$

and the boundary condition, $u=0$ at $y=h$ and also $du/dy=0$ at $y=0$. Find the velocity profile and the volume rate of flow.

解: Since $\frac{d\sigma}{dy} = \frac{\partial p}{\partial x}$, $\sigma = k|\dot{\gamma}|^n$ and $\dot{\gamma} = -\frac{du}{dy} > 0$

thus $\frac{d}{dy}\left[k\left(-\frac{du}{dy}\right)^n\right] = \frac{\partial p}{\partial x}$

Then integrating once and applying $du/dy=0$ at $y=0$, $\sigma_y = k\left(-\frac{du}{dy}\right)^n = \frac{\partial p}{\partial x}y$ and $\sigma_{max} = \frac{\partial p}{\partial x}h$

Thus, $\left(-\frac{du}{dy}\right) = \left(\frac{1}{k}\sigma_{max}\frac{y}{h}\right)^{\frac{1}{n}}$

Integrating again and apply $u=0$ at $y=h$,

$$u=\left(\frac{\sigma_{max}}{k}\right)^{\frac{1}{n}} h\frac{n}{1+n}\left[1-\left(\frac{y}{h}\right)^{\frac{1+n}{n}}\right]$$

The volume rate of flow

$$Q=2\int_0^h u dy=2\left(\frac{\sigma_{max}}{k}\right)^{\frac{1}{n}} h\frac{n}{1+n}\left[y-\frac{1}{2+\frac{1}{n}}\left(\frac{y}{h}\right)^{1+\frac{1}{n}} y\right]_0^h$$

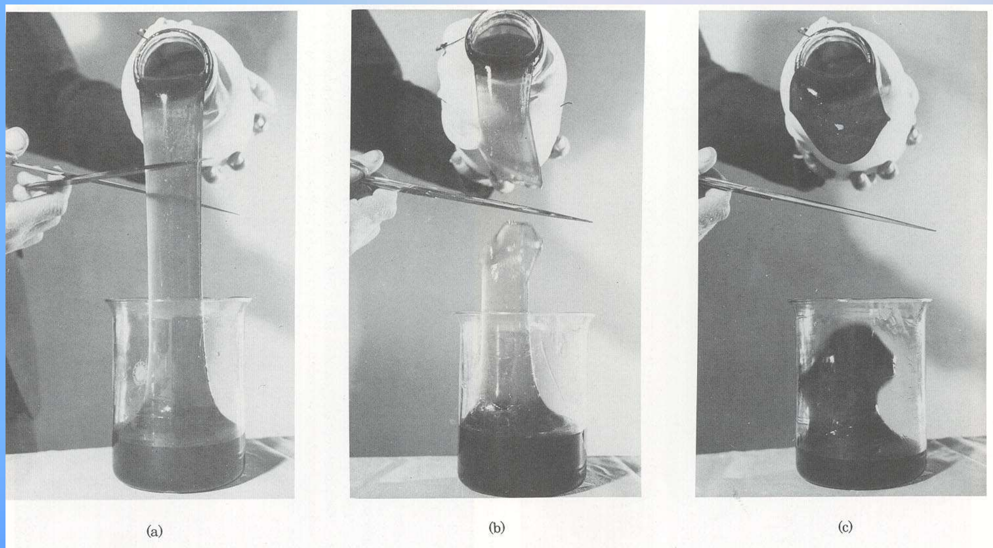
$$=\frac{2n}{2n+1}\left(\frac{\sigma_{max}}{k}\right)^{\frac{1}{n}} h^2$$

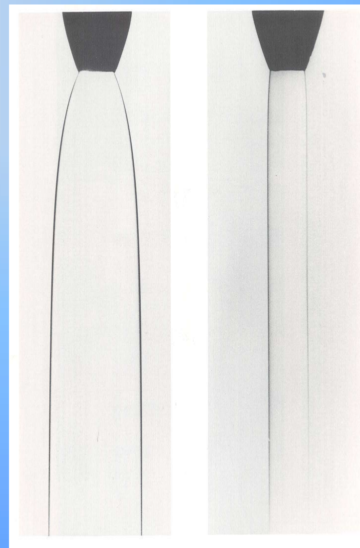
Thus, $\left(\frac{\sigma_{max}}{k}\right)^{\frac{1}{n}}=\frac{2n+1}{2n}\frac{Q}{h^2}=\frac{2n+1}{n}\frac{\bar{v}}{h}\qquad (\bar{v}=\frac{Q}{2h})$

$$u=\frac{2n+1}{1+n}\bar{v}\left[1-\left(\frac{y}{h}\right)^{\frac{1+n}{n}}\right]$$

广义牛顿流体模型的局限性

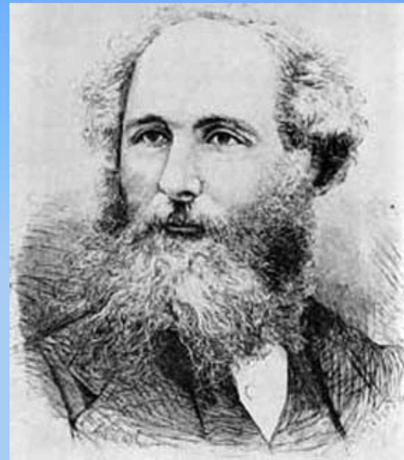
- 对于非剪切材料函数的预测是不可靠的，如拉伸粘度；
- 不能预测法向应力 N_1 和 N_2;
- 不可能预测弹性行为，如蠕变后的应变回缩等，它们取决于流体的整个变形历史。





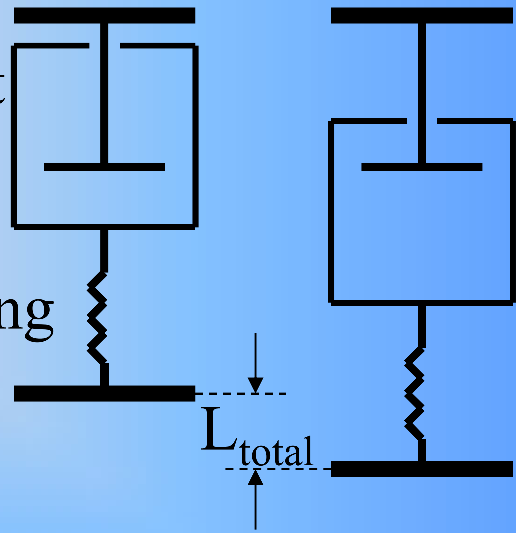
2.4 Maxwell 模型

James Clerk Maxwell 于1867年提出的第一个黏弹模型。



Hooke定律描述弹簧: $F = G_{spring}\Delta L_{spring}$

牛顿黏性定律描述黏壶: $F = \eta \frac{dL_{dash}}{dt}$



$$L_{total} = L_{spring} + L_{dash}$$

$$\frac{dL_{total}}{dt} = \frac{dL_{spring}}{dt} + \frac{dL_{dash}}{dt} = \frac{1}{G_{spring}}\frac{dF}{dt} + \frac{F}{\eta}$$

$$\therefore F + \frac{\eta}{G_{spring}}\frac{dF}{dt} = \eta\frac{dL_{total}}{dt} \quad 或 \quad \sigma + \lambda\frac{d\sigma}{dt} = \eta\dot{\gamma}$$

定常态条件下: $\frac{d\sigma}{dt} \to 0, \sigma = \eta\,\dot{\gamma}$

瞬间快速启动条件下:

$$t \to 0, \ \frac{d\sigma}{dt} >> \sigma, \ \therefore \lambda\frac{d\sigma}{dt} = \eta\dot{\gamma} \qquad \sigma = G\int_{t_{ref}}^{t}\dot{\gamma}dt' = G\gamma(t_{ref}, t)$$

微分形式： $\sigma + \lambda \frac{d\sigma}{dt} = \eta \dot{\gamma}$

$$\frac{1}{\lambda} e^{t/\lambda} \sigma + e^{t/\lambda} \frac{d\sigma}{dt} = \frac{\eta}{\lambda} e^{t/\lambda} \dot{\gamma}$$

$$\frac{\partial}{\partial t}\left(e^{t/\lambda} \sigma \right) = \frac{\eta}{\lambda} e^{t/\lambda} \dot{\gamma}$$

$$\int_{-\infty}^{t} d\left[e^{t'/\lambda} \sigma(t') \right] = \int_{-\infty}^{t} \frac{\eta}{\lambda} e^{t'/\lambda} \dot{\gamma}(t') dt'$$

积分形式：

$$\sigma(t) = e^{-t/\lambda} \int_{-\infty}^{t} \frac{\eta}{\lambda} e^{t'/\lambda} \dot{\gamma}(t') dt' = \int_{-\infty}^{t} G e^{\frac{-(t-t')}{\lambda}} \dot{\gamma}(t') dt'$$

- 应变历史： $\dot{\gamma}(t')$
- 记忆效应： $G e^{\frac{-(t-t')}{\lambda}}$

例2.3 用Maxwell本构方程预测稳态剪切条件下的物质函数。

解:

$$\sigma(t) = \int_{-\infty}^{t} \frac{\eta_0}{\lambda} e^{-\frac{t-t'}{\lambda}} \dot{\gamma}(t')dt' = \int_{-\infty}^{t} \frac{\eta_0}{\lambda} e^{-\frac{t-t'}{\lambda}} \begin{pmatrix} 0 & \dot{\gamma}_0 & 0 \\ \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} dt'$$

$$\eta \equiv \frac{\sigma_{xy}}{\dot{\gamma}_0} = \frac{1}{\dot{\gamma}_0} \int_{-\infty}^{t} \frac{\eta_0}{\lambda} e^{-\frac{t-t'}{\lambda}} \dot{\gamma}_0 dt' = \eta_0 e^{-\frac{t-t'}{\lambda}} \Big|_{-\infty}^{t} = \eta_0$$

$$\Psi_1 \equiv \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\gamma}_0^2} = 0 \qquad \Psi_2 \equiv \frac{\sigma_{yy} - \sigma_{zz}}{\dot{\gamma}_0^2} = 0$$

例2.4 用Maxwell本构方程计算稳态单轴拉伸粘度。

解：

$$\sigma(t)=\int_{-\infty}^{t}\frac{\eta_0}{\lambda}e^{-\frac{t-t'}{\lambda}}\dot{\gamma}(t')dt'=\int_{-\infty}^{t}\frac{\eta_0}{\lambda}e^{-\frac{t-t'}{\lambda}}\begin{pmatrix}-\dot{\varepsilon}_0 & 0 & 0\\ 0 & -\dot{\varepsilon}_0 & 0\\ 0 & 0 & 2\dot{\varepsilon}_0\end{pmatrix}dt'$$

$$=\underbrace{\int_{-\infty}^{t}\frac{\eta_0}{\lambda}e^{-\frac{t-t'}{\lambda}}dt'}_{\eta_0}\begin{pmatrix}-\dot{\varepsilon}_0 & 0 & 0\\ 0 & -\dot{\varepsilon}_0 & 0\\ 0 & 0 & 2\dot{\varepsilon}_0\end{pmatrix}=\begin{pmatrix}-\eta_0\dot{\varepsilon}_0 & 0 & 0\\ 0 & -\eta_0\dot{\varepsilon}_0 & 0\\ 0 & 0 & 2\eta_0\dot{\varepsilon}_0\end{pmatrix}$$

$$\eta_E\equiv\left(\sigma_{zz}-\sigma_{xx}\right)/\dot{\varepsilon}_0=\left(\sigma_{zz}-\sigma_{yy}\right)/\dot{\varepsilon}_0=3\eta_0$$

例2.5 利用Maxwell本构方程计算阶跃剪切应变条件下的物质函数。

解:

$$\dot{\gamma}_{xy}(t)=\lim_{\varepsilon\to 0}\begin{Bmatrix}0, & t<0\\ \dot{\gamma}_0, & 0\le t<\varepsilon\\ 0, & t\ge\varepsilon\end{Bmatrix}=\gamma_0\lim_{\varepsilon\to 0}\begin{Bmatrix}0, & t<0\\ \frac{1}{\varepsilon}, & 0\le t<\varepsilon\\ 0, & t\ge\varepsilon\end{Bmatrix}$$

$$\sigma_{xy}(t,\varepsilon)=\int_{-\infty}^{t}\frac{\eta_0}{\lambda}e^{-\frac{t-t'}{\lambda}}\dot{\gamma}_{xy}(t')dt'=\frac{\eta_0\gamma_0}{\lambda\varepsilon}\int_0^{\varepsilon}e^{-\frac{t-t'}{\lambda}}dt'$$

$$G(t,\gamma_0)\equiv\lim_{\varepsilon\to 0}\sigma_{xy}(t,\varepsilon)/\gamma_0=\lim_{\varepsilon\to 0}\frac{\frac{\eta_0}{\lambda}\int_0^{\varepsilon}e^{-\frac{t-t'}{\lambda}}dt'}{\varepsilon}$$

$$G_{\Psi_1}(t,\gamma_0)=(\sigma_{xx}-\sigma_{yy})/\gamma_0^2=0$$

$$G_{\Psi_2}(t,\gamma_0)=(\sigma_{yy}-\sigma_{zz})/\gamma_0^2=0$$

$$G(t)=\lim_{\varepsilon\to 0}\frac{\frac{\eta_0}{\lambda}\int_0^{\varepsilon}e^{-\frac{t-t'}{\lambda}}dt'}{\varepsilon}=\lim_{\varepsilon\to 0}\frac{\frac{\eta_0}{\lambda}\frac{d}{d\varepsilon}\int_0^{\varepsilon}e^{-\frac{t-t'}{\lambda}}dt'}{\frac{d}{d\varepsilon}\varepsilon}=\lim_{\varepsilon\to 0}\frac{\eta_0}{\lambda}e^{-\frac{t-\varepsilon}{\lambda}}$$

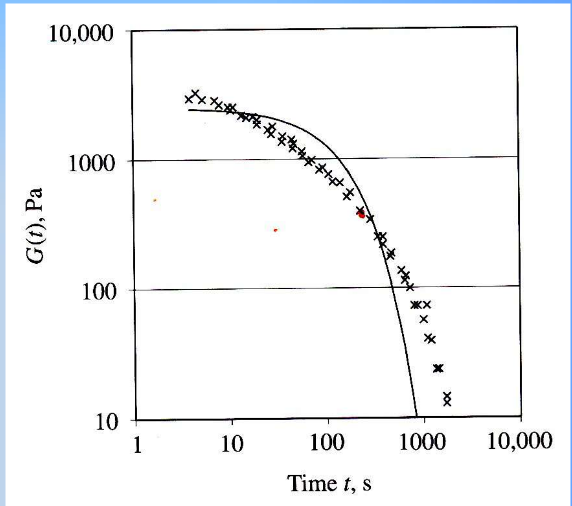
$\therefore G(t)=\frac{\eta_0}{\lambda}e^{-\frac{t}{\lambda}}$ - 松弛模量呈指数形式衰减

2.5 广义线性粘弹性本构方程及流动问题

具有众多弛豫时间的广义Maxwell模型：

$$\sigma_k + \lambda_k \frac{d\sigma_k}{dt} = \eta_k \dot{\gamma}$$

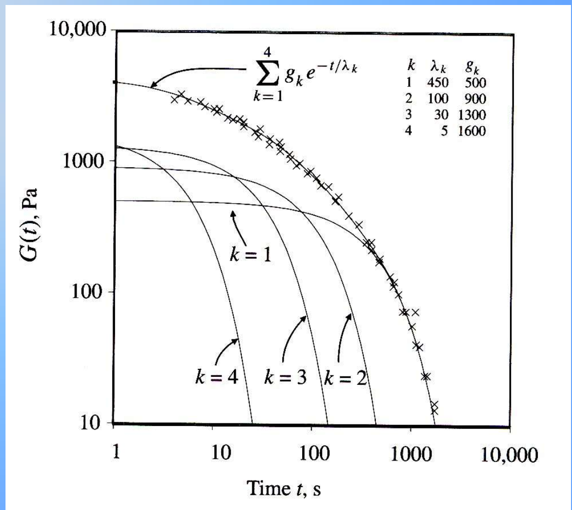
$$\sigma = \sum_{k=1}^{N} \sigma_k = \sum_{k=1}^{N} \left[\int_{-\infty}^{t} \frac{\eta_k}{\lambda_k} e^{-\frac{t-t'}{\lambda_k}} \dot{\gamma}(t') dt' \right]$$



广义线性粘弹性本构方程：

$$\sigma(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}(t') dt'$$

$$\therefore G(t) = \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{-\frac{t}{\lambda_k}}$$ - 剪切松弛模量函数



例2.6 分别用广义线性粘弹模型和广义Maxwell模型计算在小振幅剪切振荡流场下的物质函数。

解: 对样品加载一个小振幅剪切振荡应变 $\gamma(t)=\gamma_0\sin(\omega t)$

对于理想弹性体, i.e. $\sigma(t)=G\gamma(t)=G\gamma_0\sin(\omega t)$.

对于牛顿流体, $\sigma(t)=\eta\dot{\gamma}(t)=\eta\omega\gamma_0\cos(\omega t)$.

对于广义线性粘弹流体,

$$\sigma(t)=\int_{-\infty}^{t}dt'G(t-t')\dot{\gamma}(t')=\int_{-\infty}^{t}dt'G(t-t')[\omega\gamma_0\cos(\omega t')]$$

$$\xi=t-t' \quad \Rightarrow$$

$$\sigma(t)=\int_{0}^{\infty}d\xi G(\xi)[\omega\gamma_0\cos\omega(t-\xi)]$$

$$=\gamma_0\left\{\left[\omega\int_0^\infty d\xi G(\xi)\sin(\omega\xi)\right]\sin(\omega t)+\left[\omega\int_0^\infty d\xi G(\xi)\cos(\omega\xi)\right]\cos(\omega t)\right\}$$

储能模量：$G'(\omega) = \omega\int_0^\infty d\xi G(\xi)\sin(\omega\xi)$

损耗模量：$G''(\omega) = \omega\int_0^\infty d\xi G(\xi)\cos(\omega\xi)$

$$\eta'(\omega) = \int_0^\infty d\xi G(\xi)\cos(\omega\xi) = G''(\omega)/\omega$$

$$\eta''(\omega) = \int_0^\infty d\xi G(\xi)\sin(\omega\xi) = G'(\omega)/\omega. \quad \eta_0 = \lim_{\omega\to 0}\frac{G''(\omega)}{\omega} = \lim_{\omega\to 0}\eta'(\omega)$$

以广义Maxwell模型为例：$G(\xi) = G_0 e^{-\xi/\lambda}$

$$G'(\omega) = G_0\omega\int_0^\infty d\xi e^{-\xi/\lambda}\sin(\omega\xi)$$

$$= G_0\omega\frac{\omega}{1/\lambda^2+\omega^2} = \frac{G_0\omega^2\lambda^2}{1+\omega^2\lambda^2} \quad \text{or} \quad G'(\omega) = \frac{\eta_0\omega^2\lambda}{1+\omega^2\lambda^2}$$

$$G''(\omega) = G_0\omega\int_0^\infty d\xi e^{-\xi/\lambda}\cos(\omega\xi)$$

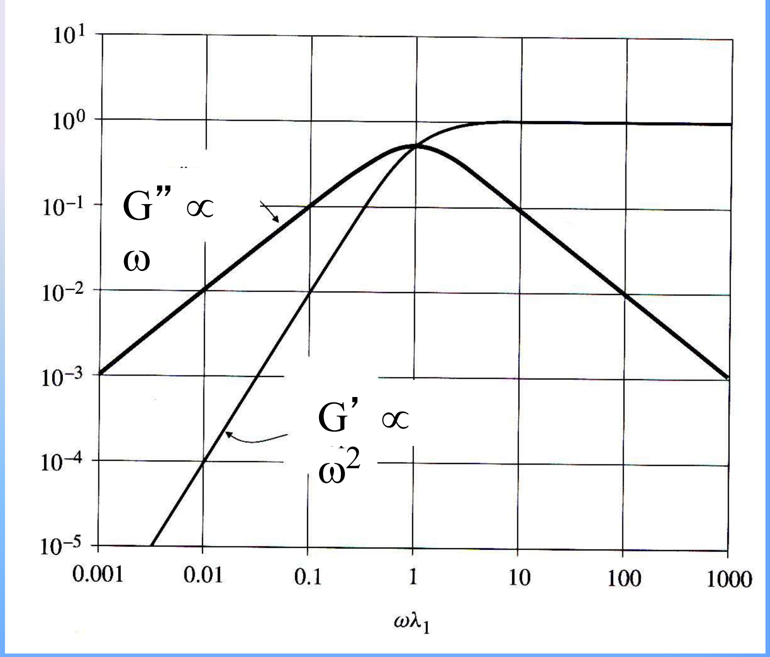
$$= G_0\omega\frac{1/\lambda}{1/\lambda^2+\omega^2} = \frac{G_0\omega\lambda}{1+\omega^2\lambda^2} \quad \text{or} \quad G''(\omega) = \frac{\eta_0\omega}{1+\omega^2\lambda^2}$$

复数模量： $G^*(\omega)=G'(\omega)+iG''(\omega)$

$$G^*(\omega)=G_0\frac{i\omega\lambda}{1+i\omega\lambda} \quad \text{or} \quad G^*(\omega)=\frac{i\omega\eta_0}{1+i\omega\lambda}$$

复数黏度： $\eta^*(\omega)=\dfrac{G^*(\omega)}{i\omega}=\eta'(\omega)-i\eta''(\omega)$

- $\omega\lambda \gg 1$, $G^*(\omega)=G_0$ → 快应变条件下，材料的弹性占主导.
- $\omega\lambda \ll 1$, $G^*(\omega)\cong i\omega G_0\lambda$ → 慢应变条件下，材料的黏性占优， $\eta_0=G_0\lambda$.



小结：广义线性粘弹模型的局限性

- 仅能预测恒定黏度（无剪切变稀），仅在小剪切率范围内适用；
- 应变累加仅在低剪切速率下有效；
- 不能预测法向应力N_1和N_2;
- 不满足参考系变化不变原则。

第三讲 – 黏弹本构方程

- 本构模型应捕获所有的非线性弹性效应；
- 应该满足旋转参照系变化不变原则。

积分形式:

$$\sigma(t)=\int_{-\infty}^{t}G(t-t')\dot{\gamma}(t')dt' \quad = G(t-t')\gamma(t,t')\Big|_{t'=-\infty}^{t'=t}-\int_{-\infty}^{t}\frac{\partial G(t-t')}{\partial t'}\gamma(t,t')dt'$$

$$=-\int_{-\infty}^{t}\frac{\partial G(t-t')}{\partial t'}\gamma(t,t')dt'=-\int_{-\infty}^{t}M(t-t')\gamma(t,t')dt'=-\int_{0}^{\infty}M(s)\gamma(t,s)ds$$

记忆函数:

$$M(t-t')=\frac{\partial G(t-t')}{\partial t'}=\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}$$

3.1 参照系变化不变原则的必要性

$$\mathbf{r} = |r|\cos\beta\,\widehat{\mathbf{e}}_x + |r|\sin\beta\,\widehat{\mathbf{e}}_y + z\widehat{\mathbf{e}}_z$$

$$\mathbf{r}' = |r|\cos(\psi+\beta)\widehat{\mathbf{e}}_x + |r|\sin(\psi+\beta)\widehat{\mathbf{e}}_y + z\widehat{\mathbf{e}}_z$$
$$= (x\cos\psi - y\sin\psi)\widehat{\mathbf{e}}_x + (x\sin\psi + y\cos\psi)\widehat{\mathbf{e}}_y + z\widehat{\mathbf{e}}_z$$

$$\mathbf{u} = \mathbf{r}' - \mathbf{r} = \begin{pmatrix} x(\cos\psi - 1) - y\sin\psi \\ x\sin\psi + y(\cos\psi - 1) \\ 0 \end{pmatrix} \qquad \nabla\mathbf{u}(t,t') = \frac{\partial u_j}{\partial x_i}\widehat{\mathbf{e}}_i\widehat{\mathbf{e}}_j = \begin{pmatrix} \cos\psi - 1 & \sin\psi & 0 \\ -\sin\psi & \cos\psi - 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\dot{\gamma}(t,t') = \left[\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right] = \begin{pmatrix} 2(\cos\psi - 1) & 0 & 0 \\ 0 & 2(\cos\psi - 1) & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\sigma(t) = -\int_{-\infty}^{t} M(t-t') \begin{pmatrix} 2(\cos\psi - 1) & 0 & 0 \\ 0 & 2(\cos\psi - 1) & 0 \\ 0 & 0 & 0 \end{pmatrix} dt'$$

!荒谬预测!

3.1.1变形梯度张量

在过去的t'时刻流体单元中的$d\mathbf{r}'$由于随单元的变形和运动在当今时刻t演化成了$d\mathbf{r}$，它们之间的关系可表达为

$$dx'(x,y,z)=\frac{\partial x'}{\partial x}dx+\frac{\partial x'}{\partial y}dy+\frac{\partial x'}{\partial z}dz=d\mathbf{r}\cdot\frac{\partial x'}{\partial \mathbf{r}}$$

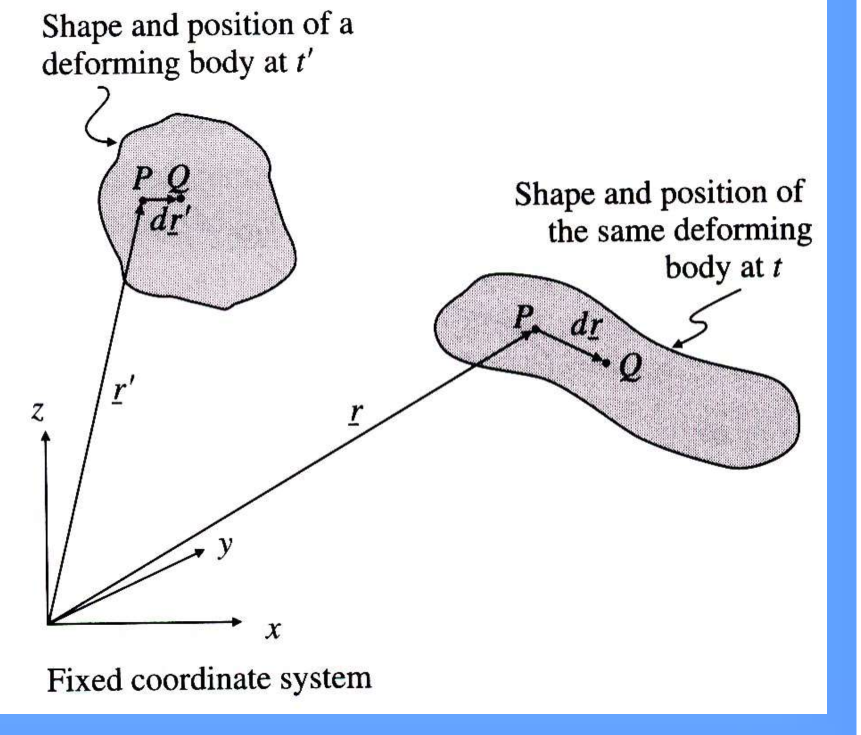
$$dy'(x,y,z)=d\mathbf{r}\cdot\frac{\partial y'}{\partial \mathbf{r}}$$

$$dz'(x,y,z)=d\mathbf{r}\cdot\frac{\partial z'}{\partial \mathbf{r}}$$

$$d\mathbf{r}'=d\mathbf{r}\cdot\frac{\partial \mathbf{r}'}{\partial \mathbf{r}}=d\mathbf{r}\cdot\mathbf{E}(t,t')$$

变形梯度张量：

$$\mathbf{E}(t,t')\equiv\frac{\partial \mathbf{r}'}{\partial \mathbf{r}}=\begin{pmatrix}\frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x}\\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y}\\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z}\end{pmatrix}$$



$$d\mathbf{r} = d\mathbf{r}' \cdot \frac{\partial \mathbf{r}}{\partial \mathbf{r}'} = d\mathbf{r}' \cdot \mathbf{E}^{-1}(t',t) \text{ 和 } \mathbf{E} \cdot \mathbf{E}^{-1} = \mathbf{I}$$

逆-变形梯度张量的时间导数：

$$\frac{\partial \mathbf{E}^{-1}}{\partial t} = \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}'} = \frac{\partial \mathbf{r}}{\partial \mathbf{r}'} \cdot \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}} = \mathbf{E}^{-1} \cdot \nabla \mathbf{v}$$

变形梯度张量的时间导数：

$$\frac{\partial \left(\mathbf{E} \cdot \mathbf{E}^{-1}\right)}{\partial t} = \mathbf{E} \cdot \frac{\partial \mathbf{E}^{-1}}{\partial t} + \frac{\partial \mathbf{E}}{\partial t} \cdot \mathbf{E}^{-1} = 0$$

$$\mathbf{E} \cdot \mathbf{E}^{-1} \cdot \nabla \mathbf{v} + \frac{\partial \mathbf{E}}{\partial t} \cdot \mathbf{E}^{-1} = 0$$

$$\nabla \mathbf{v} \cdot \mathbf{E} + \frac{\partial \mathbf{E}}{\partial t} \cdot \mathbf{E}^{-1} \cdot \mathbf{E} = \mathbf{0}$$

$$\therefore \frac{\partial \mathbf{E}}{\partial t} = -\nabla \mathbf{v} \cdot \mathbf{E}$$

3.1.2 Finger and Cauchy 应变张量

Cauchy 应变张量：$\mathbf{C}(t,t') \equiv \mathbf{E}\cdot\mathbf{E}^T$

Finger 应变张量： $\mathbf{C}^{-1}(t',t) \equiv \left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1}$

测量时间t相对于时间t'的流体构型的变形

$$\mathbf{r}(0,t) = (x'\cos\psi - y'\sin\psi)\hat{\mathbf{e}}_x + (x'\sin\psi + y'\cos\psi)\hat{\mathbf{e}}_y + z'\hat{\mathbf{e}}_z$$

$$\mathbf{E}^{-1}(t',t) \equiv \frac{\partial\mathbf{r}}{\partial\mathbf{r}'} = \begin{pmatrix} \frac{\partial x}{\partial x'} & \frac{\partial y}{\partial x'} & \frac{\partial z}{\partial x'} \\ \frac{\partial x}{\partial y'} & \frac{\partial y}{\partial y'} & \frac{\partial z}{\partial y'} \\ \frac{\partial x}{\partial z'} & \frac{\partial y}{\partial z'} & \frac{\partial z}{\partial z'} \end{pmatrix} = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \boldsymbol{\sigma}(t) = G\mathbf{C}^{-1} = G\left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1} = G\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- 刚体旋转运动不产生形变和应力。

在定常剪切的条件下：

$$\mathbf{r}(0,t)=[x'+\dot{\gamma}_0 t y']\hat{\mathbf{e}}_x+y'\hat{\mathbf{e}}_y+z'\hat{\mathbf{e}}_z$$

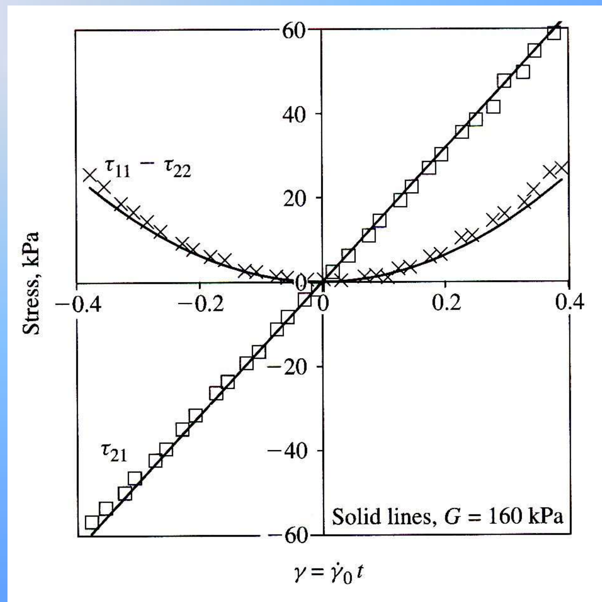
$$\mathbf{E}^{-1}=\begin{pmatrix}1&0&0\\ \dot{\gamma}_0 t&1&0\\ 0&0&1\end{pmatrix}=\begin{pmatrix}1&0&0\\ \gamma&1&0\\ 0&0&1\end{pmatrix}$$

$$\boldsymbol{\sigma}=G\mathbf{C}^{-1}=G\begin{pmatrix}1&\gamma&0\\ 0&1&0\\ 0&0&1\end{pmatrix}\cdot\begin{pmatrix}1&0&0\\ \gamma&1&0\\ 0&0&1\end{pmatrix}=G\begin{pmatrix}1+\gamma^2&\gamma&0\\ \gamma&1&0\\ 0&0&1\end{pmatrix}$$

$$\sigma_{xy}=G\gamma=G\dot{\gamma}_0 t$$

$$\sigma_{xx}-\sigma_{yy}=G\gamma^2=G\dot{\gamma}_0^2 t^2$$

$$\sigma_{yy}-\sigma_{zz}=0$$



3.2 积分形式Lodge本构方程及其对于物质函数的预测

$$\boldsymbol{\sigma}(t) = -\int_{-\infty}^{t} M(t-t')\boldsymbol{\gamma}(t,t')dt'$$

$$\Rightarrow \boldsymbol{\sigma}(t) = \int_{-\infty}^{t} M(t-t')\mathbf{C}^{-1}(t',t)dt' = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}}\right]\mathbf{C}^{-1}(t',t)dt'$$

- 积分形式的Lodge 本构方程

例3.1 利用Lodge 本构方程计算定常流条件下的剪切黏度和法向应力系数。

解: $\gamma = \dot{\gamma}_0(t-t')$

$$\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}}\right] \begin{pmatrix} 1+\left[\dot{\gamma}_0(t-t')\right]^2 & \dot{\gamma}_0(t-t') & 0 \\ \dot{\gamma}_0(t-t') & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} dt'$$

$$\sigma_{xy} = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}} \right] \dot{\gamma}_0 (t-t') dt'$$

let $\quad s = t - t', ds = -dt'; t' = -\infty, s = \infty; t' = t, s = 0$

$$\sigma_{xy} = \frac{\eta_0}{\lambda^2} \dot{\gamma}_0 \int_0^{\infty} e^{-s/\lambda} s ds$$

$$\eta = \sigma_{xy} / \dot{\gamma}_0 = \frac{\eta_0}{\lambda^2} \left[s(-\lambda) e^{-s/\lambda} \Big|_0^{\infty} + \int_0^{\infty} \lambda e^{-s/\lambda} ds \right]$$

$$= \frac{\eta_0}{\lambda^2} \left[-\lambda^2 e^{-s/\lambda} \Big|_0^{\infty} \right] = \eta_0$$

$$\sigma_{yy} = \sigma_{zz} = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}} \right] dt' = \frac{\eta_0}{\lambda^2} \int_0^{\infty} e^{-s/\lambda} ds$$

$$= \frac{\eta_0}{\lambda^2} (-\lambda) e^{-s/\lambda} \Big|_0^{\infty} = \eta_0 / \lambda$$

$$\sigma_{xx} = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}} \right] \left[1 + \left[\dot{\gamma}_0 (t - t') \right]^2 \right] dt' = \frac{\eta_0}{\lambda^2} \int_0^{\infty} e^{-s/\lambda} \left(1 + \dot{\gamma}_0^2 s^2 \right) ds$$

$$= \frac{\eta_0}{\lambda^2} \left[(-\lambda) e^{-s/\lambda} \Big|_0^{\infty} + \dot{\gamma}_0^2 \int_0^{\infty} e^{-s/\lambda} s^2 ds \right]$$

$$= \frac{\eta_0}{\lambda^2} \left[\lambda + \dot{\gamma}_0^2 \left(-s^2 \lambda e^{-s/\lambda} \Big|_0^{\infty} + 2\lambda \int_0^{\infty} e^{-s/\lambda} s ds \right) \right]$$

$$= \frac{\eta_0}{\lambda^2} \left[\lambda + \dot{\gamma}_0^2 2\lambda \left(s(-\lambda) e^{-s/\lambda} \Big|_0^{\infty} + \int_0^{\infty} \lambda e^{-s/\lambda} ds \right) \right]$$

$$= \frac{\eta_0}{\lambda} \left[1 + \dot{\gamma}_0^2 2 \left(-\lambda^2 e^{-s/\lambda} \Big|_0^{\infty} \right) \right] = \frac{\eta_0}{\lambda} \left[1 + 2 \dot{\gamma}_0^2 \lambda^2 \right]$$

$$\Psi_1 \equiv \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\gamma}_0^2} = 2\eta_0 \lambda \qquad \Psi_2 \equiv \frac{\sigma_{yy} - \sigma_{zz}}{\dot{\gamma}_0^2} = 0$$

3.3 微分形式的Lodge方程以及随流导数

前面已经得到：
$$\frac{\partial \mathbf{E}^{-1}}{\partial t} = \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}'} = \frac{\partial \mathbf{r}}{\partial \mathbf{r}'} \cdot \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}} = \mathbf{E}^{-1} \cdot \nabla \mathbf{v}$$

$$\frac{\partial (\mathbf{E}^{-1})^T}{\partial t} = \left[\mathbf{E}^{-1} \cdot \nabla \mathbf{v}\right]^T = \left(\nabla \mathbf{v}\right)^T \cdot \left(\mathbf{E}^{-1}\right)^T$$

于是,

$$\frac{\partial}{\partial t}\mathbf{C}^{-1}(t',t) = \frac{\partial}{\partial t}\left[\left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1}\right] = \frac{\partial}{\partial t}\left[\left(\mathbf{E}^{-1}\right)^T\right] \cdot \mathbf{E}^{-1} + \left(\mathbf{E}^{-1}\right)^T \cdot \frac{\partial}{\partial t}\left[\mathbf{E}^{-1}\right]$$
$$= \left(\nabla \mathbf{v}\right)^T \cdot \left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1} + \left(\mathbf{E}^{-1}\right)^T \cdot \mathbf{E}^{-1} \cdot \nabla \mathbf{v}$$
$$= \left(\nabla \mathbf{v}\right)^T \cdot \mathbf{C}^{-1} + \mathbf{C}^{-1} \cdot \nabla \mathbf{v}$$

根据 $\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{t-t'}{\lambda}}\right] \mathbf{C}^{-1}(t',t)dt'$ 计算 $d\boldsymbol{\sigma}/dt$

（其中利用Leibnitz 规则对积分求导）。

$$\frac{d\boldsymbol{\sigma}(t)}{dt}=\frac{d}{dt}\left\{\int_{-\infty}^{t}\left[\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}\right]\mathbf{C}^{-1}(t',t)dt'\right\}$$

$$=\int_{-\infty}^{t}\frac{\partial}{\partial t}\left[\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}\mathbf{C}^{-1}(t',t)\right]dt'+\left[\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}\mathbf{C}^{-1}(t',t)\right]_{t'=t}$$

$$=\int_{-\infty}^{t}\left[\frac{\eta_0}{\lambda^2}\left(-\frac{1}{\lambda}\right)e^{-\frac{t-t'}{\lambda}}\mathbf{C}^{-1}(t',t)\right]dt'+\int_{-\infty}^{t}\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}\frac{\partial}{\partial t}\mathbf{C}^{-1}(t',t)dt'+\frac{\eta_0}{\lambda^2}\mathbf{I}$$

$$=-\frac{1}{\lambda}\boldsymbol{\sigma}(t)+\int_{-\infty}^{t}\frac{\eta_0}{\lambda^2}e^{-\frac{t-t'}{\lambda}}\left[\left(\nabla\mathbf{v}\right)^T\cdot\mathbf{C}^{-1}+\mathbf{C}^{-1}\cdot\nabla\mathbf{v}\right]dt'+\frac{\eta_0}{\lambda^2}\mathbf{I}$$

$$=-\frac{1}{\lambda}\boldsymbol{\sigma}+\left(\nabla\mathbf{v}\right)^T\cdot\boldsymbol{\sigma}+\boldsymbol{\sigma}\cdot\nabla\mathbf{v}+\frac{\eta_0}{\lambda^2}\mathbf{I}$$

整理后: $\boldsymbol{\sigma}+\lambda\left[\frac{d\boldsymbol{\sigma}(t)}{dt}-\left(\nabla\mathbf{v}\right)^T\cdot\boldsymbol{\sigma}-\boldsymbol{\sigma}\cdot\nabla\mathbf{v}\right]=\frac{\eta_0}{\lambda}\mathbf{I}$

再定义“上随流导数”为: $\overset{\nabla}{\boldsymbol{\sigma}}\equiv\frac{D\boldsymbol{\sigma}}{Dt}-\left(\nabla\mathbf{v}\right)^T\cdot\boldsymbol{\sigma}-\boldsymbol{\sigma}\cdot\nabla\mathbf{v}$

微分形式的Lodge方程: $\boldsymbol{\sigma}+\lambda\overset{\nabla}{\boldsymbol{\sigma}}=\frac{\eta_0}{\lambda}\mathbf{I}$

Lodge本构方程的微分形式： $\boldsymbol{\sigma} + \lambda \overset{\nabla}{\boldsymbol{\sigma}} = \frac{\eta_0}{\lambda} \mathbf{I}$

再令 $\boldsymbol{\Xi} = \boldsymbol{\sigma} - \frac{\eta_0}{\lambda} \mathbf{I}$ ，这一方程可写成：

$$\boldsymbol{\Xi} + \frac{\eta_0}{\lambda} \mathbf{I} + \lambda \overset{\nabla}{\boldsymbol{\Xi}} + \eta_0 \overset{\nabla}{\mathbf{I}} = \frac{\eta_0}{\lambda} \mathbf{I}$$

和 $\overset{\nabla}{\mathbf{I}} \equiv -\left[(\nabla \mathbf{v})^T + \nabla \mathbf{v} \right]$

于是， $\boldsymbol{\Xi} + \lambda \overset{\nabla}{\boldsymbol{\Xi}} = \eta_0 \left[(\nabla \mathbf{v})^T + \nabla \mathbf{v} \right]$

或 $\boldsymbol{\sigma} + \lambda \overset{\nabla}{\boldsymbol{\sigma}} = \eta_0 \left[(\nabla \mathbf{v})^T + \nabla \mathbf{v} \right]$

对于任意一个张量**A**, 它的“上随流导数”定义为

$$\overset{\nabla}{\mathbf{A}} \equiv \frac{D\mathbf{A}}{Dt} - (\nabla \mathbf{v})^T \cdot \mathbf{A} - \mathbf{A} \cdot \nabla \mathbf{v}$$

物理意义:

- 从随流动而变化的坐标系中度量任一张量的变化率，该坐标系随流体平移、旋转和变形；
- 满足参考系变化不变原则。

"下随流导数"被定义为：$\overset{\Delta}{\mathbf{A}} \equiv \frac{D\mathbf{A}}{Dt} + \nabla\mathbf{v}\cdot\mathbf{A} + \mathbf{A}\cdot(\nabla\mathbf{v})^T$

"共旋导数"：

$$\overset{\circ}{\mathbf{A}} \equiv \frac{D\mathbf{A}}{Dt} + \frac{1}{2}\left[\underbrace{\left[\nabla\mathbf{v} - (\nabla\mathbf{v})^T\right]}_{\boldsymbol{\omega}}\cdot\mathbf{A} - \mathbf{A}\cdot\left[\nabla\mathbf{v} - (\nabla\mathbf{v})^T\right]\right]$$

"Gordon-Schowalter 导数"：

$$\frac{\delta\sigma}{\delta t} = \xi\overset{\Delta}{\sigma} + (1-\xi)\overset{\nabla}{\sigma}$$

$$= \frac{\partial\sigma}{\partial t} + \mathbf{v}\cdot\nabla\sigma + \sigma\cdot\left[\xi(\nabla\mathbf{v})^T - (1-\xi)\nabla\mathbf{v}\right] + \left[\xi\nabla\mathbf{v} - (1-\xi)(\nabla\mathbf{v})^T\right]\cdot\sigma$$

3.4 广义非线性粘弹性本构模型

微分形式:

$$\frac{\delta\sigma}{\delta t}+\frac{1}{\lambda}\sigma+\Theta(\sigma,\dot{\gamma})=G\left[\nabla\mathbf{v}+\left(\nabla\mathbf{v}\right)^{T}\right]$$

1. Johnson-Segalman 模型 - 0<ξ<1 和 $\Theta(\sigma,\dot{\gamma})=\mathbf{0}$

2. Giesekus 模型 ξ=0 和 $\Theta(\sigma,\dot{\gamma})=\alpha\frac{1}{G\lambda}\sigma\cdot\sigma$

3. Phan-Thien & Tanner 模型 ξ=0 和

$$\boldsymbol{\Theta}(\boldsymbol{\sigma},\dot{\boldsymbol{\gamma}})=\frac{1}{\lambda}\left[exp\left[\frac{\alpha}{G}\operatorname{tr}(\boldsymbol{\sigma})\right]-1\right]\boldsymbol{\sigma}$$

4. Larson 模型 ξ=0 和 $\Theta(\sigma,\dot{\gamma})=\frac{\alpha}{3G}\left[\nabla\mathbf{v}+\left(\nabla\mathbf{v}\right)^{T}\right]:\ \sigma\left(\sigma+G\mathbf{I}\right)$

积分形式:

$$\boldsymbol{\sigma}(t)=\int_{-\infty}^{t} M(t-t')\left[\varphi_1(I_1,I_2)\mathbf{C}^{-1}(t',t)+\varphi_2(I_1,I_2)\mathbf{C}(t,t')\right]dt'$$

若是 $\varphi_1(I_1,I_2)\equiv 2\frac{\partial U}{\partial I_1}$ 和 $\varphi_1(I_1,I_2)\equiv -2\frac{\partial U}{\partial I_2}$

K-BKZ 模型:

$$\boldsymbol{\sigma}(t)=\int_{-\infty}^{t} M(t-t')\left[2\frac{\partial U}{\partial I_1}\mathbf{C}^{-1}(t',t)-2\frac{\partial U}{\partial I_2}\mathbf{C}(t,t')\right]dt'$$

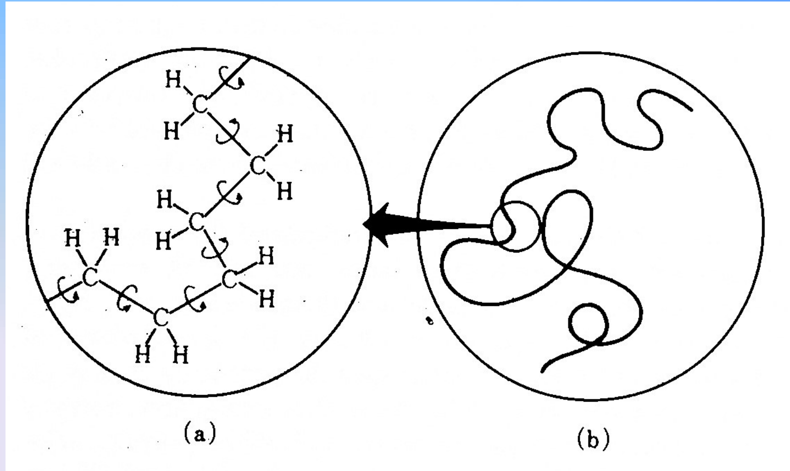
第四讲 - 微观本构模型

4.1 聚合物分子理论基础

等效高斯链模型

其有效键长b，具有高斯分布:

$$\psi(\mathbf{r}) = \left[\frac{3}{2\pi b^2}\right]^{3/2} exp\left(-\frac{3\mathbf{r}^2}{2b^2}\right)$$



离散高斯链的

构象分布函数：$\Psi(\{\mathbf{r}_n\}) = \prod_{n=1}^{N}\left[\frac{3}{2\pi b^2}\right]^{3/2} exp\left[-\frac{3\mathbf{r}_n^2}{2b^2}\right]$

$$= \left[\frac{3}{2\pi b^2}\right]^{3N/2} exp\left[-\sum_{n=1}^{N}\frac{3(\mathbf{R}_n - \mathbf{R}_{n-1})^2}{2b^2}\right]$$

连续高斯链的

构象分布函数：$\Psi[\mathbf{R}_n] = const\ exp\left[-\frac{3}{2b^2}\int_0^N dn\left(\frac{\partial \mathbf{R}_n}{\partial n}\right)^2\right]$

Sir Sam F. Edwards
(1928-2015)

在外场$U_e(\mathbf{r})$ 的作用下，高斯链的构象分布函数是：

$$\Psi[\mathbf{R}_n] \propto exp\left[-\frac{3}{2b^2}\int_0^N dn\left(\frac{\partial \mathbf{R}_n}{\partial n}\right)^2 - \frac{1}{k_B T}\int_0^N dn U_e(\mathbf{R}_n)\right]$$

定义Green 函数：

$$G(\boldsymbol{R}, \boldsymbol{R}';N) \equiv \frac{\int_{\mathbf{R}_0=\mathbf{R}'}^{\mathbf{R}_N=\mathbf{R}} \delta \mathbf{R}_n \, exp\left[-\frac{3}{2b^2}\int_0^N dn\left(\frac{\partial \mathbf{R}_n}{\partial n}\right)^2 - \frac{1}{k_B T}\int_0^N dn U_e(\mathbf{R}_n)\right]}{\int d\mathbf{R} \int_{\mathbf{R}_0=\mathbf{R}'}^{\mathbf{R}_N=\mathbf{R}} \delta \mathbf{R}_n \, exp\left[-\frac{3}{2b^2}\int_0^N dn\left(\frac{\partial \mathbf{R}_n}{\partial n}\right)^2\right]}$$

包含所有构象的配分函数是：

$$\Omega = \int d\mathbf{R}\, d\mathbf{R}'\, G(\mathbf{R}, \mathbf{R}'; N).$$

利用 $G(\boldsymbol{R}, \boldsymbol{R}';N)$ 就可以计算任何一个物理量，如

$$\langle A(\mathbf{R}_n)\rangle = \frac{\int d\,\mathbf{R}_N\, d\,\mathbf{R}_n\, d\,\mathbf{R}_0\, G(\mathbf{R}_N,\mathbf{R}_n;N-n)\,G(\mathbf{R}_n,\mathbf{R}_0;n)\,A(\mathbf{R}_n)}{\int d\,\mathbf{R}_N\, d\,\mathbf{R}_0\, G(\mathbf{R}_N,\mathbf{R}_0;N)}$$

而 Green 函数满足如下偏微分方程,

$$\left(\frac{\partial}{\partial n}-\frac{b^2}{6}\frac{\partial^2}{\partial \mathbf{R}^2}+\frac{1}{k_BT}U_e(\mathbf{R})\right)G(\mathbf{R},\mathbf{R}';n)=\delta(\mathbf{R}-\mathbf{R}')\delta(n) \qquad (0\le n\le N)$$

$$\frac{U_e(\mathbf{R})}{k_BT}=\upsilon_0(1-2\chi)\rho(\mathbf{R})$$

和 $$\rho(\mathbf{R})=\frac{\int_0^N dn\,G(\mathbf{R},\mathbf{R}';n)\int d\,\mathbf{R}''\,G(\mathbf{R}'',\mathbf{R};N-n)}{\int d\,\mathbf{R}''\,G(\mathbf{R}'',\mathbf{R}';N)}$$

在θ温度或浓溶液条件下，$U_e = 0$, $G(\boldsymbol{R}, \boldsymbol{R}'; N)$约化为高斯分布函数，$G_0(\mathbf{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 exp\left(-\beta^2 R^2\right)$

其中 $\beta^2 \equiv \frac{3}{2Nb^2}$ ，并且 $R^2 = \mathbf{R}\cdot\mathbf{R}$ 于是

$$\left\langle R^2 \right\rangle_0 \equiv \int_0^\infty R^2 G_0(\mathbf{R}) \cdot 4\pi R^2 dR = \frac{3}{2\beta^2} = Nb^2$$

当$U_e \neq 0$时, 考虑某个**R**链构象的自由能是

$$\mathbf{A}(\mathbf{R}) = -k_B T ln G(\mathbf{R}, N) + 与\ \mathbf{R}\ 无关的项$$

$$\cong k_B T \left(\frac{3R^2}{2Nb^2} + \upsilon(T) \frac{N^2}{R^{\mathrm{d}}} \right)$$

平衡态下 $\partial \mathbf{A}/\partial R = 0$, $\left\langle R^2 \right\rangle_0 \propto N^{2\nu}$. 当$d=3$时, $\nu=0.6$.

重整化群计算的结果：$\nu=0.592$.

更精确计算的结果： $\nu = 0.588 \pm 0.001$.

高分子的应力张量

单分子链力：$\mathbf{F}^s=\dfrac{\partial A}{\partial \mathbf{R}}=-T\dfrac{\partial S}{\partial \mathbf{R}}=2k_BT\beta^2\mathbf{R}$

对于多链 N_s 系统：$\boldsymbol{\sigma}^p=\dfrac{1}{V}\sum_{i=1}^{N_s}\mathbf{R}_i\mathbf{F}_i^s=c\left\langle \mathbf{R}\mathbf{F}^s\right\rangle$

对于Gaussian链：$\boldsymbol{\sigma}^p=2k_BTc\beta^2\left\langle \mathbf{R}\mathbf{R}\right\rangle$

- 高分子的应力源自其构象分布在外力场作用下的变化；
- 对于高斯链，它与分布函数的二阶矩成正比；
- 机械应力与分子取向的各向异性有关。

对于拥有 N 个链段的高分子：

$$\sigma_{\alpha\beta}^p=\frac{c}{N}\frac{3k_BT}{b^2}\sum_{n=1}^{N}\left\langle(\mathbf{R}_{n+1}-\mathbf{R}_n)_\alpha(\mathbf{R}_{n+1}-\mathbf{R}_n)_\beta\right\rangle$$

$$=\frac{c}{N}\frac{3k_BT}{b^2}\int_0^N dn\left\langle\frac{\partial R_{n\alpha}}{\partial n}\frac{\partial R_{n\beta}}{\partial n}\right\rangle$$

4.2 Brownian运动基础理论

描述一个小圆球（半径=a）悬浮在一个已知黏度（ η ）和密度（ ρ ）溶液中的布朗运动是动量守恒方程，Langevin 方程:

Particle inertia + the viscous drag = the fluctuating Brownian force

$$m\frac{d^2x}{dt^2}+\zeta\frac{dx}{dt}=f\left(t\right)$$

其中 $x(t)$ 是球心位置，其质量 $m=4\pi a^3\rho/3$.

- 初始条件： $x(0)=0$ 和 $v(t=-\infty)=\frac{d\mathbf{x}}{dt}=0$, 即$t=0$， 系统达到平衡态；
- 特征时间分离假设（ Einstein ）：快速涨落的Brownian力 (水 ~10^{-13} 秒) 与慢得多的黏性阻力.
- 布朗力在方向和大小上完全随机，在小圆球运动时间尺度上不相关。

Brownian力满足：

$$\langle f(t)\rangle = 0 \quad \text{and} \quad \langle f(t+s)f(t)\rangle = F\delta(s)$$

其中 δ(*s*) 是delta函数

求解Langevin 方程：$\frac{dv}{dt}+\frac{\zeta}{m}v=\frac{1}{m}f(t)$

或 $\frac{1}{m}\left[\zeta v - f(t)\right]dt + dv = 0$

利用积分因子 $\mu(t)=e^{\frac{\zeta}{m}t}$

$$\frac{d}{dt}\left[ve^{\frac{\zeta}{m}t}\right]=\frac{1}{m}f(t)e^{\frac{\zeta}{m}t}$$

$$\therefore \quad v(t)=\frac{dx}{dt}=\frac{1}{m}\int_{-\infty}^{t}f(t')e^{-\frac{\zeta}{m}(t-t')}dt'$$

速度自相关函数：

$$C(s)=\langle v(t+s)v(t)\rangle=\frac{1}{m^2}\int_{-\infty}^{t+s}dt'\int_{-\infty}^{t}dt''e^{-\frac{\zeta}{m}(t+s-t')}e^{-\frac{\zeta}{m}(t-t'')}\langle f(t')f(t'')\rangle$$

$$=\frac{1}{m^2}\int_{-\infty}^{t+s}dt'\int_{-\infty}^{t}dt''e^{-\frac{\zeta}{m}(2t+s-t'-t'')}F\delta(t'-t'')$$

$$=\frac{F}{m^2}\int_{-\infty}^{t}dt''e^{-\frac{\zeta}{m}(2t+s-2t'')}=\frac{F}{m^2}\frac{m}{2\zeta}e^{-\frac{\zeta}{m}(2t+s-2t'')}\Big|_{-\infty}^{t}=\frac{F}{2\zeta m}e^{-\frac{\zeta}{m}s}$$

- 速度自相关函数以简单的指数形式衰减，其松弛时间是：

$$\lambda_v=\frac{m}{\zeta}=\frac{m}{6\pi\eta a}=\frac{2\rho a^2}{9\eta}$$

- Brownian 颗粒具有短记忆 ， 对于水中a=0. 1μm的小球$\lambda_V=10^{-9}$秒。在黏性时间尺度上，由每个热脉冲传递给小球的能量独立衰减。

根据平衡态统计力学平均动能均分原理：

$$\frac{1}{2}m\left\langle \frac{dx}{dt}\frac{dx}{dt}\right\rangle = \frac{1}{2}k_BT \qquad \therefore F = 2\zeta k_BT$$

- 随机Brownian力波动的强度与耗散能量的黏性力联系起来。

关于Brownian运动颗粒位置的方程：

$$m\frac{d^2x}{dt^2} + \zeta\frac{dx}{dt} = f(t)$$

$$mx\frac{d^2x}{dt^2} + \zeta x\frac{dx}{dt} = xf(t)$$

$$\frac{m}{2}\frac{d^2(x^2)}{dt^2} - mv^2 + \frac{\zeta}{2}\frac{d(x^2)}{dt} = xf(t)$$

关于颗粒位置均方$<x^2>$的方程:

$$\frac{m}{2}\frac{d^2<x^2>}{dt^2} + \frac{\zeta}{2}\frac{d<x^2>}{dt} = k_BT$$

重排: $$\frac{d^2<x^2>}{dt^2}+\frac{\zeta}{m}\frac{d<x^2>}{dt}=\frac{2k_BT}{m}$$

求解: $$\frac{d}{dt}\left[\frac{d<x^2>}{dt}e^{\frac{\zeta}{m}t}\right]=\frac{2k_BT}{m}e^{\frac{\zeta}{m}t}$$

$$\frac{d<x^2>}{dt}e^{\frac{\zeta}{m}t}=\frac{2k_BT}{m}\frac{m}{\zeta}e^{\frac{\zeta}{m}t}+c$$

关于$<x^2>$的通解: $$\frac{d<x^2>}{dt}=\frac{2k_BT}{\zeta}+ce^{-\frac{\zeta}{m}t}$$

在长时间条件下, 第二项可忽略，并再积分一次:

$$<x^2>=\frac{2k_BT}{\zeta}t=2Dt$$

著名的 **Einstein** 公式: $$D=\frac{k_BT}{\zeta}$$

系统的热涨落 ⇔ 系统在外力作用下的响应

For $t >> \frac{\rho a^2}{\eta}$ and $\langle \mathbf{x}^2 \rangle = a^2,\ t=\frac{6\pi\eta a^3}{k_BT}$ ≈10^{-3} s for a=0.1μm.

Brownian 运动的另一种数学描述是**Smoluchowski** 方程,
即关于概率分布函数, $\Psi(\mathbf{x},t)$, 随时间的演化方程:

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial \mathbf{x}} \frac{1}{\zeta} \left(k_B T \frac{\partial \Psi}{\partial \mathbf{x}} + \frac{\partial U}{\partial \mathbf{x}} \Psi \right) = \frac{\partial}{\partial \mathbf{x}} D \left(\frac{\partial \Psi}{\partial \mathbf{x}} + \frac{1}{k_B T} \frac{\partial U}{\partial \mathbf{x}} \Psi \right)$$

- 第一项表示由于Brownian运动引起的扩散;
- 第二项表示由外部势能驱动的漂移或对流;
- 若 U 与时间无关，且边界上没有通量,

当 $t \to \infty$, $\Psi \propto exp(-U/k_B T)$

4.3 弹性哑铃模型

若是忽略惯性，弹性哑铃在牛顿溶剂中的动量守恒方程：

$$\frac{1}{2}\zeta\left(\dot{\mathbf{R}}-\mathbf{R}\cdot\nabla\mathbf{v}\right)+2k_BT\beta^2\mathbf{R}+k_BT\frac{\partial\, ln\Psi}{\partial\mathbf{R}}=0$$

从上式关于$\dot{\mathbf{R}}$的表达式代入以下连续方程，

$$\frac{\partial\Psi}{\partial t}+\frac{\partial}{\partial\mathbf{R}}\cdot\left(\dot{\mathbf{R}}\Psi\right)=0$$

得到关于弹性哑铃概率分布函数的Smoluchowski方程，

$$\frac{\partial\Psi}{\partial t}+\frac{\partial}{\partial\mathbf{R}}\cdot\left[\mathbf{R}\cdot\nabla\mathbf{v}\Psi-\frac{4k_BT\beta^2}{\zeta}\mathbf{R}\Psi-\frac{2k_BT}{\zeta}\frac{\partial\Psi}{\partial\mathbf{R}}\right]=0$$

等式两边乘以 **RR** 并对**R**坐标积分：

$$\int \frac{\partial \Psi}{\partial t}\mathbf{RR}\, d\,\mathbf{R} = \frac{\partial}{\partial t}\langle \mathbf{RR} \rangle$$

$$\int \mathbf{RR}\frac{\partial}{\partial \mathbf{R}} \cdot \left(\mathbf{R}\cdot\nabla\mathbf{v}\Psi\right) d\,\mathbf{R} = -\nabla\mathbf{v}^{T}\cdot\langle \mathbf{RR} \rangle - \langle \mathbf{RR} \rangle\cdot\nabla\mathbf{v}$$

$$-\frac{4k_B T\beta^2}{\zeta}\int \mathbf{RR}\frac{\partial}{\partial \mathbf{R}}\cdot\left(\mathbf{R}\Psi\right) d\,\mathbf{R} = \frac{8k_B T\beta^2}{\zeta}\langle \mathbf{RR} \rangle$$

$$-\frac{2k_B T}{\zeta}\int \mathbf{RR}\frac{\partial}{\partial \mathbf{R}}\cdot\frac{\partial \Psi}{\partial \mathbf{R}} d\,\mathbf{R} = -\frac{4k_B T}{\zeta}\delta$$

利用 $\boldsymbol{\sigma}^{p} = 2k_B T c\beta^2\langle \mathbf{RR} \rangle$ 和 $\beta^2 = \dfrac{3}{2Nb^2}$

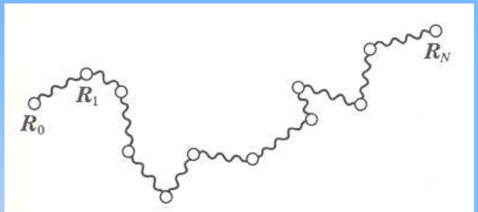
$$\therefore \quad \dot{\boldsymbol{\sigma}}^{p} - \nabla\mathbf{v}^{T}\cdot\boldsymbol{\sigma}^{p} - \boldsymbol{\sigma}^{p}\cdot\nabla\mathbf{v} + \frac{1}{\lambda}\left(\boldsymbol{\sigma}^{p} - G\delta\right) = 0$$

- 重现上对流 **Maxwell** 模型，其中 $G=ck_B T$ 和 $\lambda = \dfrac{\zeta}{8k_B T\beta^2}$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{p} + \boldsymbol{\sigma}^{s} \quad \text{其中} \quad \boldsymbol{\sigma}^{s} = \eta\left(\nabla\mathbf{v} + \nabla\mathbf{v}^{T}\right)$$

- **Oldroyd-B**模型

4.4 Rouse Model （1953年）



以**Smoluchowski**方程描述：

$$\frac{\partial \Psi}{\partial t}=\frac{\partial}{\partial \mathbf{x}}\frac{1}{\zeta}\left(k_B T\frac{\partial \Psi}{\partial \mathbf{x}}+\frac{\partial U}{\partial \mathbf{x}}\Psi\right)\Rightarrow\frac{\partial \Psi}{\partial t}=\sum_n\frac{\partial}{\partial \mathbf{R}_n}\cdot\mathbf{H}_{nm}\cdot\left(k_B T\frac{\partial \Psi}{\partial \mathbf{R}_m}+\frac{\partial U}{\partial \mathbf{R}_m}\Psi\right)$$

其中 $\mathbf{H}_{nm}=\frac{\mathrm{I}}{\zeta}\delta_{nm}$ and $U=\frac{k}{2}\sum_{n=1}^{N}\left(\mathbf{R}_n-\mathbf{R}_{n-1}\right)^2$ $\quad with\ k=\frac{3k_B T}{b^2}$

以**Langevin**方程描述：

$$\frac{d\mathbf{R}_n}{dt}=\frac{k}{\zeta}\left(\mathbf{R}_{n+1}+\mathbf{R}_{n-1}-2\mathbf{R}_n\right)+\mathbf{g}_n \qquad n=0,1,2,\ldots,\mathrm{N}.$$

其中 $\mathbf{R}_{-1}\equiv\mathbf{R}_0$ 和 $\mathbf{R}_{N+1}\equiv\mathbf{R}_N$ 。若写成连续变量形式：

$$\frac{\partial \mathbf{R}(n,t)}{\partial t}=\frac{k}{\zeta}\frac{\partial^2\mathbf{R}(n,t)}{\partial n^2}+\mathbf{g}(n,t)$$

当 $n=0$ or $n=N$, $\frac{\partial \mathbf{R}}{\partial n}=0$

对**Langevin**方程进行正交坐标转换：

$$\mathbf{X}_p(t)=\frac{1}{N}\int_0^N dn\,cos\left(\frac{p\pi n}{N}\right)\mathbf{R}(n,t)$$ 可得到：

$$\frac{d\mathbf{X}_p}{dt}=-\frac{k_p}{\zeta_p}\mathbf{X}_p+\mathbf{g}_p$$

其中 $\zeta_0=N\zeta$ 以及 $\zeta_p=2N\zeta$ 当 p=1,2,…

$$k_p=\frac{2\pi^2 k}{N}p^2=\frac{6\pi^2 k_B T}{Nb^2}p^2$$ 当 p=0,1,2,…

$$\langle g_{p\alpha}(t)\rangle=0$$ 和 $$\langle g_{p\alpha}(t)g_{q\beta}(t')\rangle=2\frac{k_BT}{\zeta_p}\delta_{pq}\delta_{\alpha\beta}\delta(t-t')$$

求解 $\mathbf{X}_p$ 得到：

$$\mathbf{X}_p(t)=\int_{-\infty}^{t}dt'\,\mathbf{g}_p(t')exp\left(-\frac{k_p(t-t')}{\zeta_p}\right)$$

计算时间相关函数

$$\langle \mathbf{X}_{p\alpha}(t)\mathbf{X}_{q\beta}(0)\rangle = \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' exp\left[-\frac{k_p(t-t'-t'')}{\zeta_p}\right]\langle g_{p\alpha}(t')g_{q\beta}(t'')\rangle$$

$$= \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' exp\left[-\frac{k_p(t-t'-t'')}{\zeta_p}\right]\frac{2k_BT}{\zeta_p}\delta_{pq}\delta_{\alpha\beta}\delta(t'-t'')$$

$$= \delta_{pq}\delta_{\alpha\beta}\frac{k_BT}{k_p}exp(-t/\lambda_p)$$

其中 $\lambda_p = \frac{\zeta_p}{k_p} = \frac{\lambda_1}{p^2} = \frac{1}{p^2}\frac{\zeta N^2 b^2}{3\pi^2 k_B T}$ 当 p=1,2,…

当 p>0, $\mathbf{X}_p$表示链的局部运动(N/p 链段以及$\sqrt{Nb^2/p}$ 链段长度)

当 p=0,

$$\left\langle \left(\mathbf{X}_0(t)-\mathbf{X}_0(0)\right)_\alpha \left(\mathbf{X}_0(t)-\mathbf{X}_0(0)\right)_\beta \right\rangle = \delta_{\alpha\beta}\frac{2k_BT}{\zeta_0}t$$

再求$\mathbf{X}_p$的逆变换 $\mathbf{X}_p(t)=\int_{-\infty}^{t}dt'\,\mathbf{g}(t')\,exp\left(-\frac{k_p(t-t')}{\zeta_p}\right)$ 得到：

$$\mathbf{R}_n=\mathbf{X}_0+2\sum_{p=1}^{\infty}\mathbf{X}_p\,cos\left(\frac{p\pi n}{N}\right)$$

Rouse 链的质心位置：$\mathbf{R}_G\equiv\frac{1}{N}\int_0^N dn\,\mathbf{R}_n=\mathbf{X}_0$

$\mathbf{R}_G$ 的均方位移：

$$\left\langle\left(\mathbf{R}_G(t)-\mathbf{R}_G(0)\right)^2\right\rangle=\sum_{\alpha=x,y,z}\left\langle\left(\mathbf{X}_{0\alpha}(t)-\mathbf{X}_{0\alpha}(0)\right)^2\right\rangle=6\frac{k_BT}{N\zeta}t$$

$$D_G=\frac{k_BT}{N\zeta}\propto M^{-1}\quad 和\quad \lambda_1=\frac{\zeta N^2b^2}{3\pi^2k_BT}\propto M^2$$

实验结果: $D_G\propto M^{-\nu}$ 和 $\lambda_1\propto M^{3\nu}$

4.5 Zimm 模型（1956）

考虑流体动力相互作用的影响

$$\frac{d\mathbf{R}_n}{dt} = \sum_m \mathbf{H}_{nm} \cdot k \frac{\partial^2 \mathbf{R}_m}{\partial m^2} + \mathbf{g}_n$$

其中 $\mathbf{H}_{nn} = \frac{\mathbf{I}}{\zeta}$ *and* $\mathbf{H}_{nm} = \frac{1}{8\pi\eta|\mathbf{r}_{nm}|}\left[\hat{\mathbf{r}}_{nm}\hat{\mathbf{r}}_{nm} + \mathbf{I}\right]$ *for* $n \neq m$

引入近似：$\mathbf{H}_{nm} \Rightarrow \langle \mathbf{H}_{nm} \rangle_{eq} \equiv \int d\{\mathbf{R}_n\} \mathbf{H}_{nm} \Psi_{eq}(\{\mathbf{R}_n\})$

$$= \frac{1}{8\pi\eta}\left\langle \frac{1}{|\mathbf{r}_{nm}|} \right\rangle_{eq} \left\langle \hat{\mathbf{r}}_{nm}\hat{\mathbf{r}}_{nm} + \mathbf{I} \right\rangle_{eq}$$

$$= h(n-m)\mathbf{I}$$

在 θ 溶剂条件下：$h(n-m) = \frac{1}{\sqrt{6\pi^3 |n-m|}\, b\eta}$

分子链的运动方程可写成：

$$\frac{\partial \mathbf{R}(n,t)}{\partial t} = k\int_0^N dm\, h(n-m)\frac{\partial^2 \mathbf{R}(m,t)}{\partial m^2} + \mathbf{g}(n,t)$$

$\mathbf{g}(n,t)$的相关函数是：

$$\langle g_\alpha(n,t)\, g_\beta(m,t)\rangle = 2\,h(n-m)\,k_B T\,\delta_{\alpha\beta}\delta(t-t')$$

进行正交坐标转换

$$\frac{d\,\mathbf{X}_p}{dt} = -\sum_q h_{pq}k_q\,\mathbf{X}_q + \mathbf{g}_p$$

其中 $k_p = \frac{2\pi^2 k}{N}p^2 = \frac{6\pi^2 k_B T}{Nb^2}p^2\ (p=0,1,2,\ldots)$

$$h_{pq} = \frac{1}{N^2}\int_0^N dn \int_0^N dm \cos\left(\frac{p\pi n}{N}\right)\cos\left(\frac{p\pi m}{N}\right) h(n-m)$$

$$\cong \frac{1}{\eta\sqrt{12\pi^3 N b^2 p}}\delta_{pq}$$

从而获得与Rouse模型相同的形式：

$$\frac{d\mathbf{X}_p}{dt} = -\frac{k_p}{\zeta_p}\mathbf{X}_q + \mathbf{g}_p$$ 其中 $\zeta_p \equiv \frac{1}{h_{pp}} = \eta\sqrt{12\pi^3 N b^2 p}$ ，当 $p>0$

当 $p=0$， $\zeta_0 = \left[\frac{1}{N^2}\int_0^N dn \int_0^N dm\, h(n-m)\right]^{-1} = \frac{3}{8}\eta\sqrt{6\pi^3 N}\, b$

于是得到：

$$D_G = \frac{k_B T}{\zeta_0} = \frac{8 k_B T}{3\eta\sqrt{6\pi^3 N}\, b} \propto M^{-1/2} \qquad \lambda_1 = \frac{\zeta_1}{k_1} = \frac{\eta N^{3/2} b^3}{(3\pi)^{1/2} k_B T} \propto M^{3/2}$$

若是在良溶剂条件下：$\left\langle \frac{1}{|\mathbf{r}_{nm}|} \right\rangle \approx \frac{1}{|n-m|^{\nu} b}$

$\zeta_0 \cong \eta N^{\nu} b$ 和 $\zeta_p \cong \eta N^{\nu} b p^{1-\nu}$ （$p>0$）

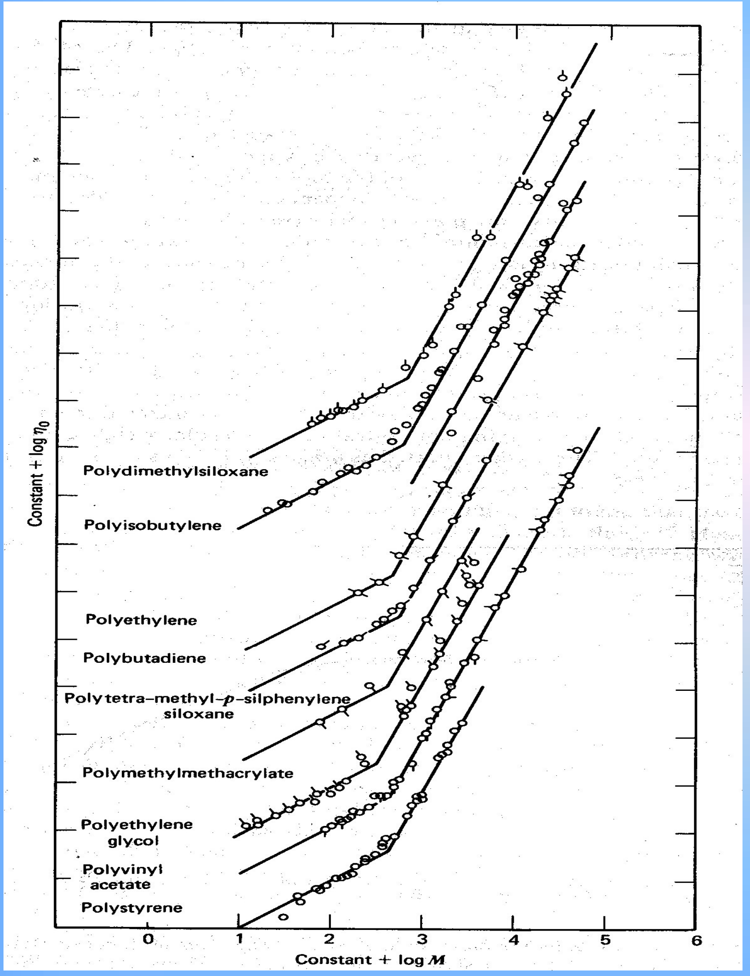
$k_0 = 0$ 和 $k_p = \frac{3 k_B T}{\left\langle \mathbf{X}_p^2 \right\rangle_{eq}} \cong \frac{k_B T p^{2\nu+1}}{N^{2\nu} b^2}$ （$p>0$）

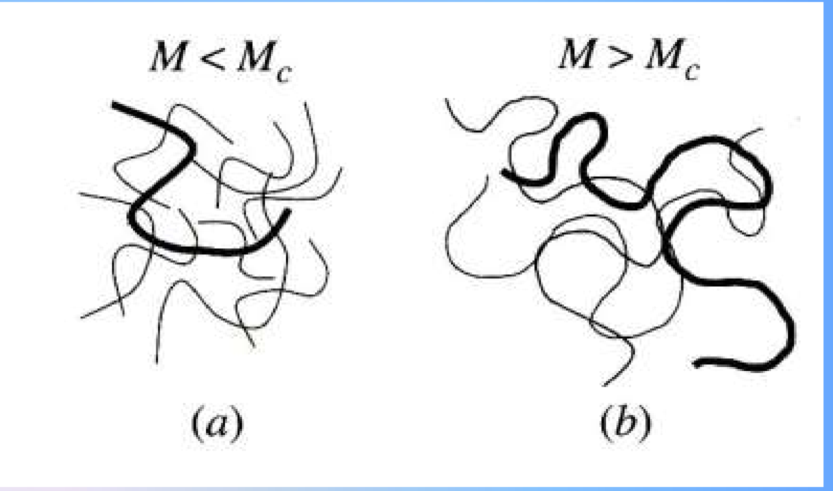
于是：

$$D_G = \frac{k_B T}{\zeta_0} = \frac{k_B T}{\eta N^{\nu} b} \propto \mathbf{R}_g^{-1}$$

$$\lambda_1 = \frac{\zeta_1}{k_1} = \frac{\eta N^{3\nu} b^3}{k_B T} \propto \mathbf{R}_g^{\ 3}$$

4.6 缠结高分子动力学





$$\eta_0 \propto M \qquad (M < M_c)$$

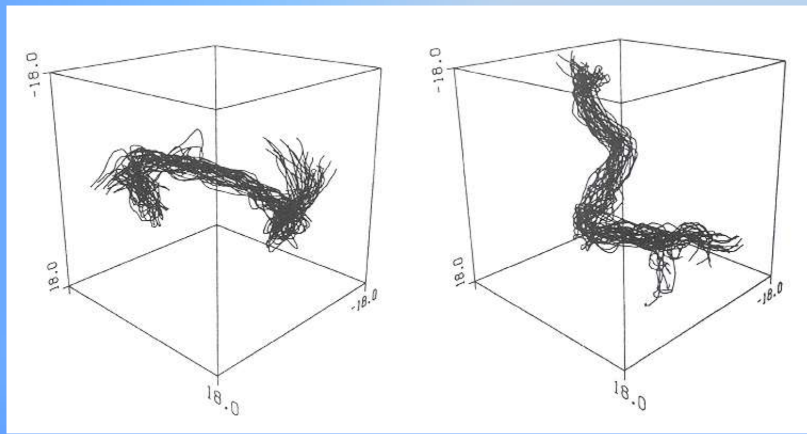
$$\eta_0 \propto M^{3.4} \qquad (M > M_c)$$

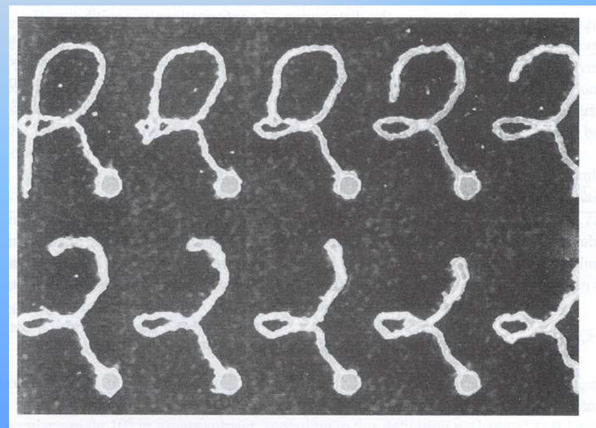
4.6.1 缠结效应以及管状模型

- **F. Burche (1952):** 缠结效应→ η ~ $N^{3.5}$
- **S.F. Edwards (1967):**

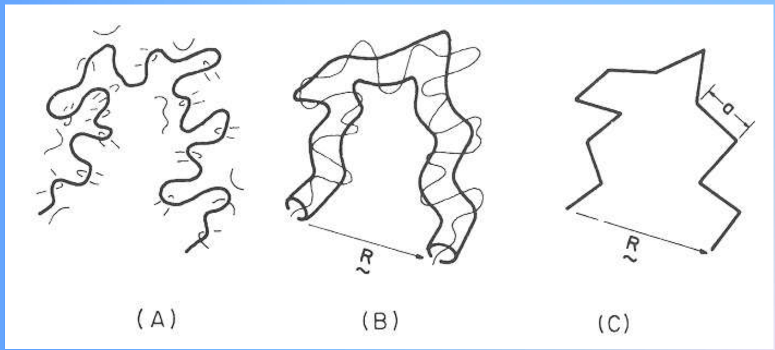
  "管状模型" – 直径：$a=F$ [density, stiffness, NOT N]
- **P.G. de Gennes (1971):** "蠕动"模型 （链分子在三维固定网络，对于熔融高分子体系 "More complicated"）
- **M. Doi and S.F. Edwards (1978)**:

  "管状模型" + "蠕动" 模型 → 完整的高分子动力学理论





“管状模型”有不同的表达形式（结果相似）：



A) 滑移链: $L=N'a$

B) 光滑壁管 ： L=长度 and a=直径

C) 原始链: $La=\langle R_0^2\rangle_{pri.chain}=\langle R_0^2\rangle_{chain}$

$$N_{primi.chain}=\frac{L}{a}\approx\frac{N_{chain}}{N_e}=\frac{M}{M_e}$$

$$L=N_{primi.chain}a=\langle R_0^2\rangle_{chain}/a=N_{chain}b^2/a$$

链张力: $\mathbf{f}=3k_BTL\hat{\mathbf{u}}/R_0^2$

4.6.2 蠕动 (受限在曲线管的扩散过程)

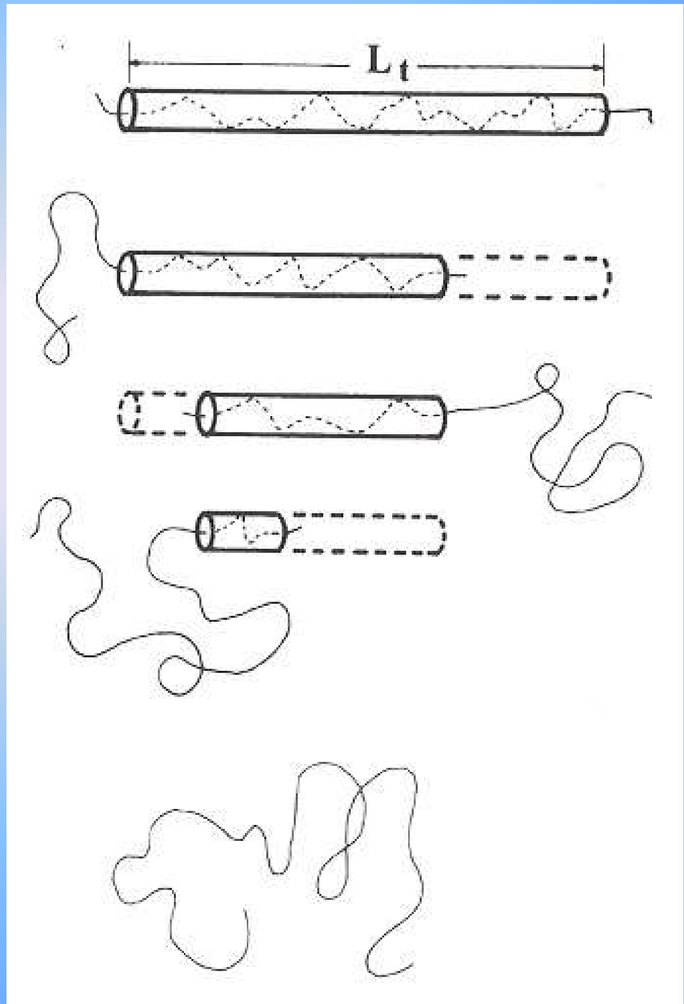
基本假设:

- 原始链长度固定L =>忽略波动。
- 原始链在管道内遵循Rouse链动力学，其中扩散系数

$$D_c = \frac{k_B T}{N\zeta}$$

- 切线向量$\mathbf{u}(s, t)=\partial \mathbf{R}(s,t)/\partial s$ 和 $\mathbf{u}(s',t)= \partial \mathbf{R}(s',t)/\partial s'$ 的相关性随着 |s-s'| 快速降低=> 在大尺度下呈现Gaussian链行为, i.e. 当 $|s-s'|>>a$.

$$\left\langle \left(\mathbf{R}(s,t)-\mathbf{R}(s',t)\right)^2 \right\rangle = a|s-s'|$$



计算向量$\mathbf{P}(t)\equiv\mathbf{R}(L,t)-\mathbf{R}(0,t)$ 的时间相关函数：

$$\langle \mathbf{P}(t)\mathbf{P}(0)\rangle = a\langle L(t)\rangle = a\int_0^L ds\,\psi(s,t)$$

其中 $\psi(s,t)$是某段原始链s在t 时刻仍保留在原始管中的生存概率

令 $\Psi(\xi, t; s)$ 是当原始链移动一个ξ 距离时原始管链段s在原始管中的生存概率。它满足一维扩散方程：

$$\frac{\partial \Psi}{\partial t} = D_c \frac{\partial^2 \Psi}{\partial \xi^2}$$

其中初始条件：$\Psi(\xi, t; s)=\delta(\xi)$

边界条件：$\Psi(\xi, t; s)=0$ at $\xi=s$ and $\xi=s-L$

求解后得到：

$$\Psi(\xi,t;s) = \sum_{p=1}^{\infty}\frac{2}{L}sin\left(\frac{p\pi s}{L}\right)sin\left(\frac{p\pi(s-\xi)}{L}\right)exp\left(-\frac{p^2 t}{\lambda_d}\right)$$

其中 $\lambda_d = \dfrac{L^2}{D_c\pi^2}$

原始链段s存活的概率：

$$\psi(s,t)=\int_{s-L}^{s} d\xi\Psi(\xi,t;s)=\sum_{p;odd}\frac{4}{p\pi}sin\left(\frac{p\pi s}{L}\right)exp\left(-\frac{p^2 t}{\lambda_d}\right)$$

归一化后的生存概率：

$$\psi(t)=\frac{1}{L}\int_0^L ds\,\psi(s,t)=\sum_{p;odd}\frac{8}{p^2\pi^2}exp\left(-\frac{p^2 t}{\lambda_d}\right)$$

于是,

$$\langle \mathbf{P}(t)\mathbf{P}(0)\rangle = La\,\psi(t)=Nb^2\,\psi(t)=Nb^2\sum_{p;oed}\frac{8}{p^2\pi^2}exp\left(-\frac{p^2 t}{\lambda_d}\right)$$

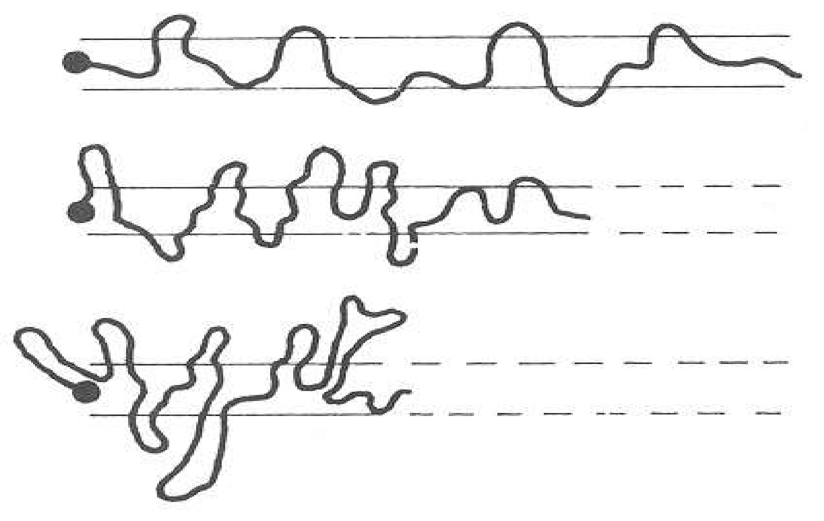
蠕动松弛时间：

$$\lambda_d=\frac{L^2}{D_c\pi^2}=\frac{1}{\pi^2}\frac{\zeta N^3 b^4}{k_B T a^2}\propto M^3 \qquad \text{Also}\quad \frac{\lambda_d}{\lambda_R}=3N_{primi.chain}$$

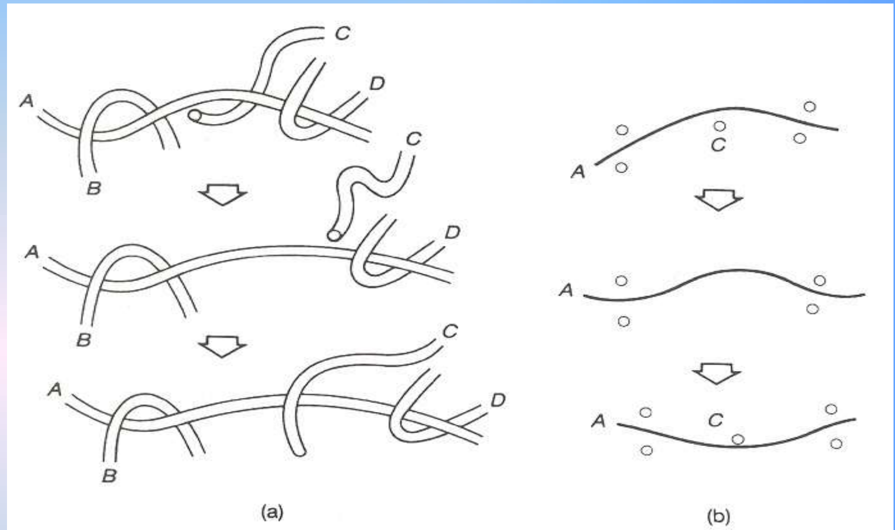
分子模型的进一步改进

- 引入非蠕动松弛机理

原始链的涨落



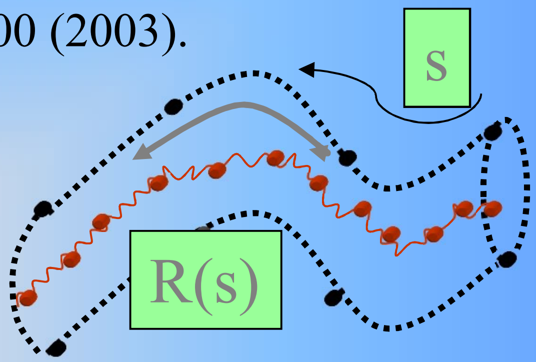
约束释放



- 消除IA近似
- 引入枝化和多分散的因素
- 流场下聚合物相变（结晶）动力学和结构演化

Detailed Chain Formulation (GLAMM model)

Graham, Likhtman, Milner, TCBM, J. Rheol, 47, 1171-1200 (2003).



$$f(s,s',t) \equiv \left\langle \frac{\partial R(s,t)}{\partial s}\frac{\partial R(s',t)}{\partial s'} \right\rangle; \quad \sigma \propto \int_0^z f(s,s)\,ds$$

Reptation +CLF

flow

CR

$$\frac{\partial f}{\partial t} = \left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right) D(s,s')\left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right)(f-f_{eq}) + \kappa f + f\kappa^T + \frac{3\nu}{2}\left(\frac{\partial^2}{\partial s^2}+\frac{\partial^2}{\partial s'^2}\right)(f-f_{eq})$$
$$+\frac{1}{2\pi^2\tau_e}\left(\frac{\partial}{\partial s} f(s,s')\frac{\partial}{\partial s}\left(\ln\left(tr\, f(s,s)\right)\right) + \frac{\partial}{\partial s'} f(s,s')\frac{\partial}{\partial s'}\left(\ln\left(tr\, f(s',s')\right)\right)\right)$$

retraction

Turning Neutrons towards Doi-Edwards Theory

PRL **95,** 166001 (2005) PHYSICAL REVIEW LETTERS week ending 14 OCTOBER 2005

Small Angle Neutron Scattering Observation of Chain Retraction after a Large Step Deformation

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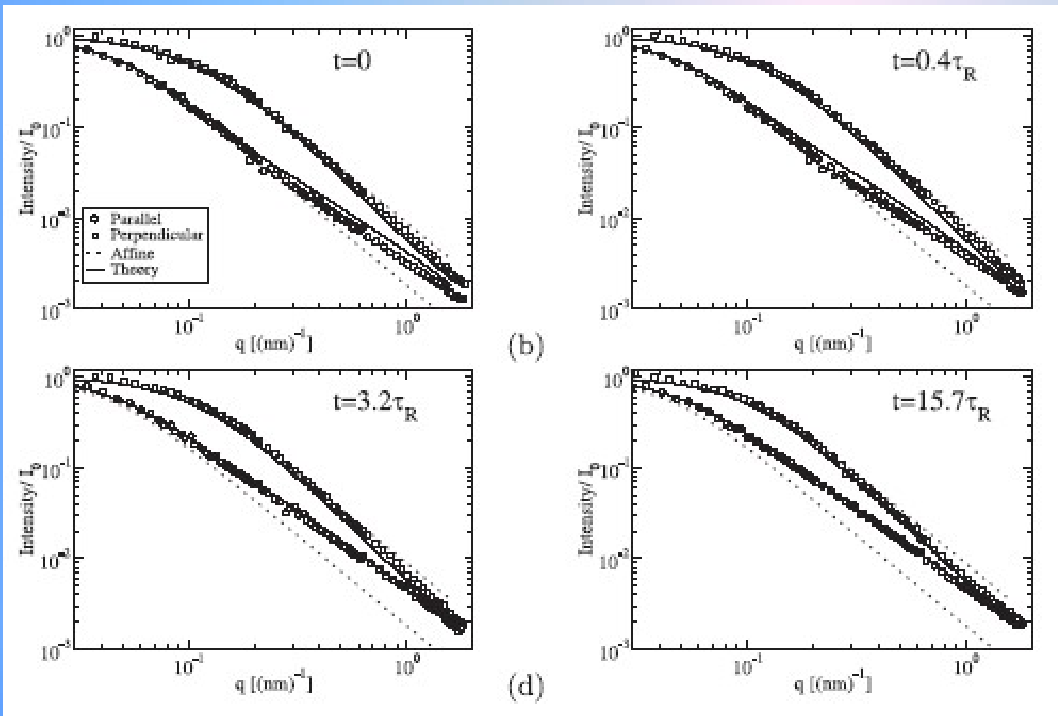

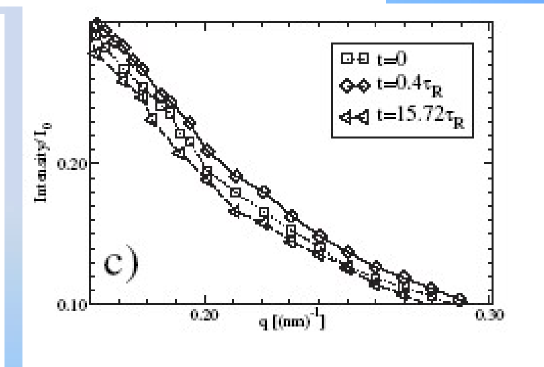

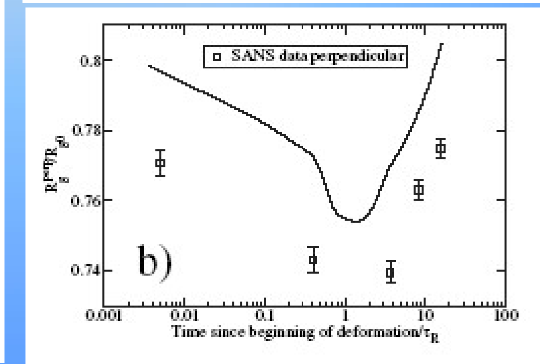

H-polymer melt relaxation with neutrons

μPP²

Small-Angle Neutron Scattering Study of the Relaxation of a Melt of Polybutadiene H-Polymers Following a Large Step Strain

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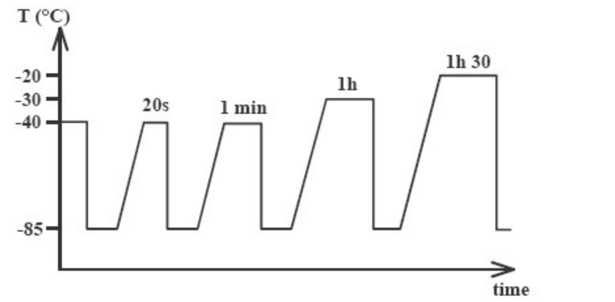
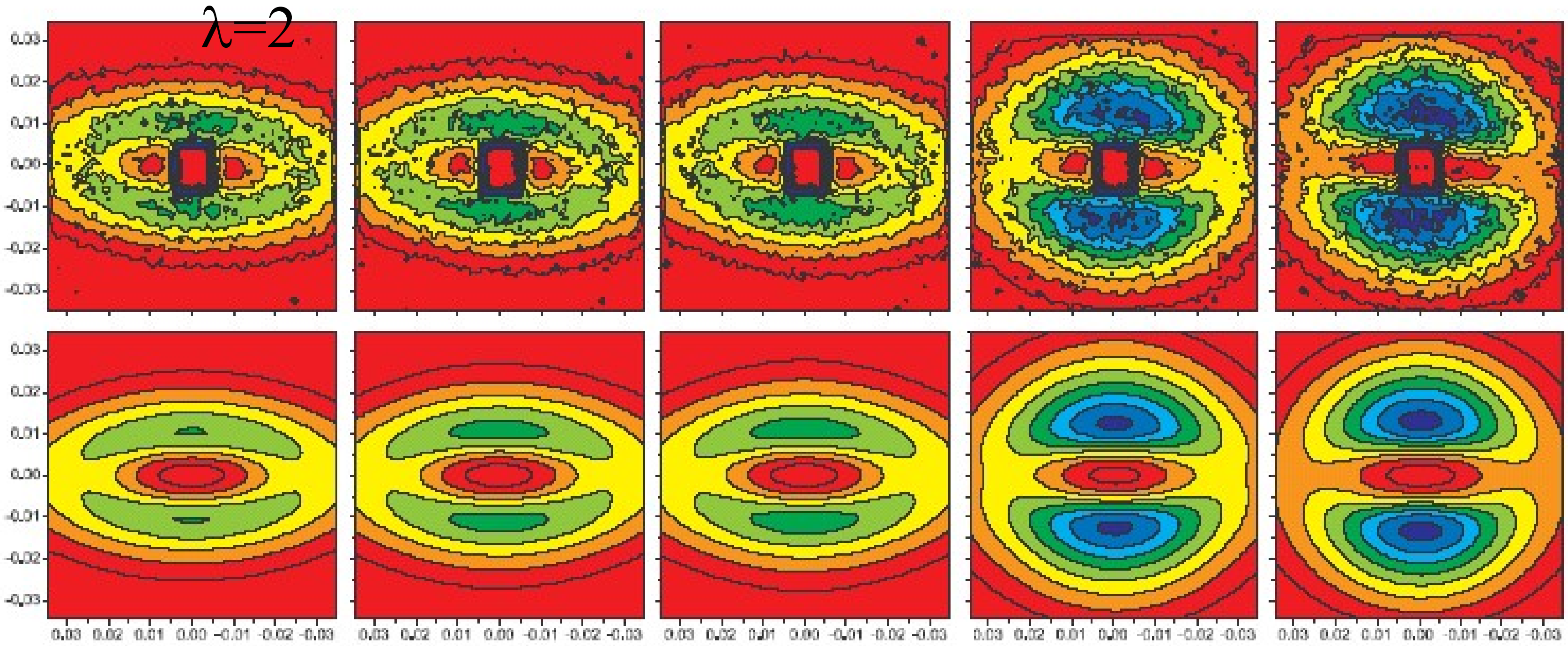
Received August 21, 2003





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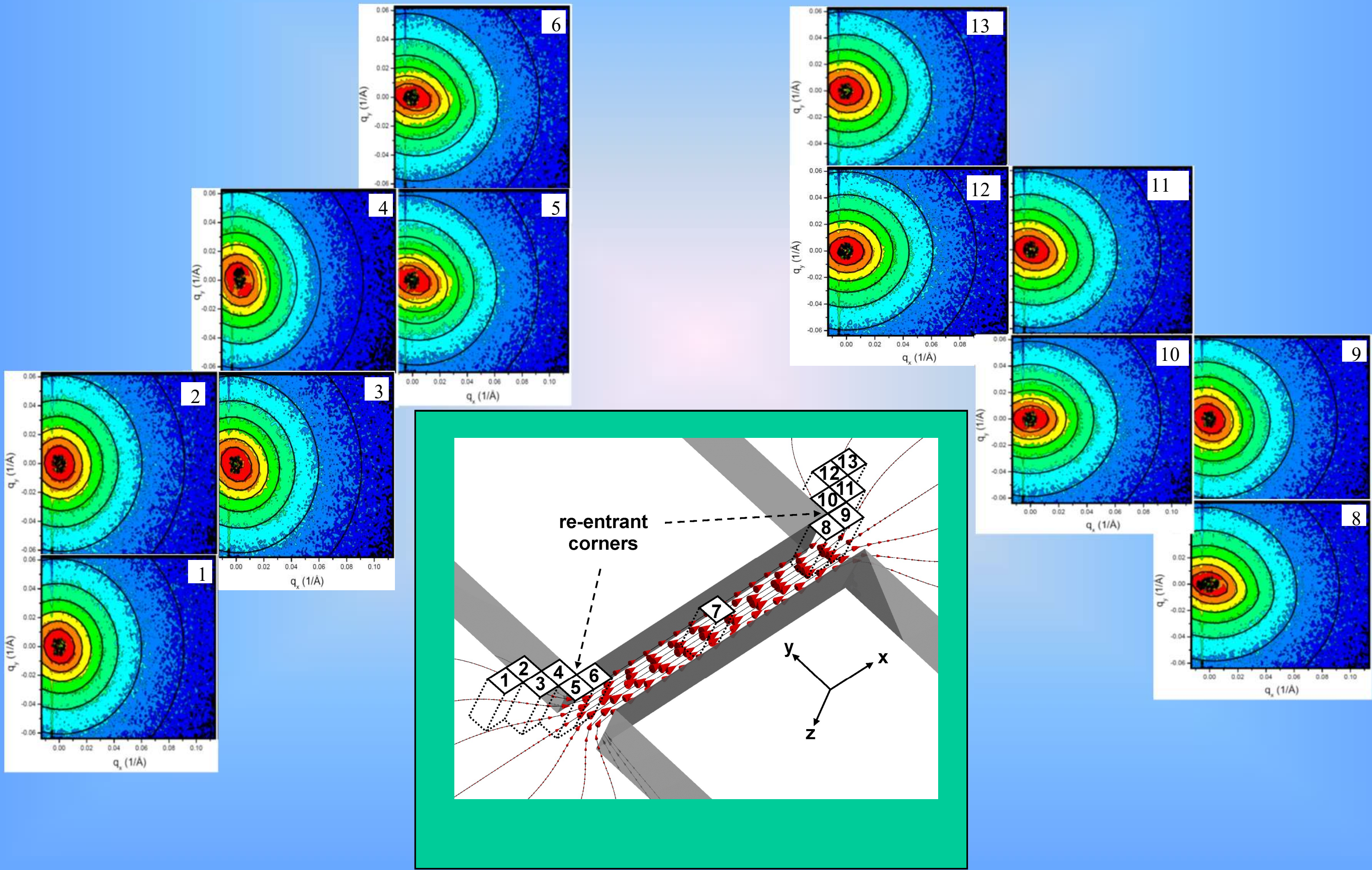
SANS Total Flow Mapping

μPP²



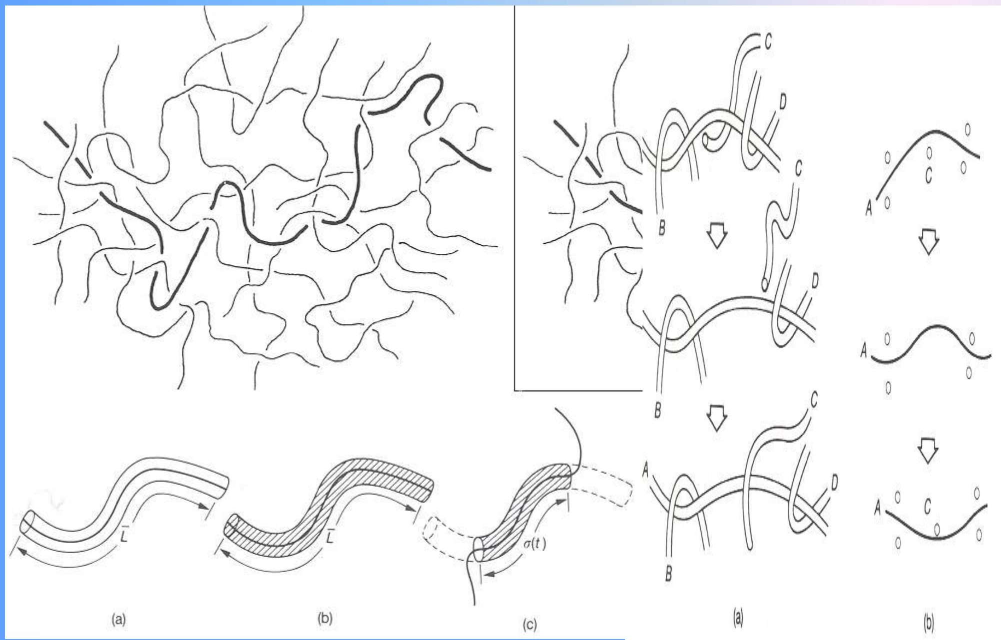
T. Gough, J. Bent, R. Richards, N. Clarke, E. de Luca, P. Coates,

A Unified Molecular Model (SCFT + Reptation Dynamics)

Doi & Edwards (1978); Shima, Kuni, Okabe, Doi, Yuan & Kawakatsu (2003)

$$\left\{\frac{\partial}{\partial n}-\frac{1}{2}\nabla\nabla:\mathbf{S}(n,\mathbf{r})+\frac{1}{k_BT}V(\mathbf{r})\right\}G(n,\mathbf{r};n',\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')\delta(n-n')$$

$$\mathbf{S}\equiv\langle\mathbf{uu}\rangle \qquad \boldsymbol{\sigma}(\mathbf{r})=\frac{3k_BT}{a^2}\int_0^N\mathbf{S}(n,\mathbf{r})\,dn-p(\mathbf{r})\boldsymbol{\delta}$$



1. Advection of the segments.
2. Deformation of the chain.
3. Chain retraction after a large deformation.
4. Thermal diffusion of the chain in the tube – (biased) reptation.
5. Constraint release (or double reptation).
6. Convective constraint release.

智能制造工程研究院

复杂流体多尺度计算模拟--科学与工业应用挑战

2018高等培训研讨会

时间： 2018年9月25日9：00开始，9月28日中午12：00结束

语言： 英语

地点： 广州大学智能制造工程研究院、系统流变学研究所
广州市番禺区大学城信息枢纽大楼10楼会议室

1. **Professor Masao Doi**: Variational Principle in Soft Matter Dynamics
2. **Professor Tim Phillips**: Mathematical and Computational Modelling of Complex Fluids and Benchmark Problems in Computational Rheology
3. **Professor Toshihiro Kawakatsu**: Multiscale Simulation Methods in Complex Fluids and Dynamics of Polymer/Surfactant Systems
4. **Professor Wenbin Hu:** Monte Carlo Simulations of Polymer Crystallization: from Fundamentals to Applications
5. **…**

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