Chapter 7 Constitutive Equations from Molecular Theories

7.1-1 Hookean elastic dumbbell

$$\underline{F}^{c} = H\underline{R} \quad (7.1\text{-}1)$$

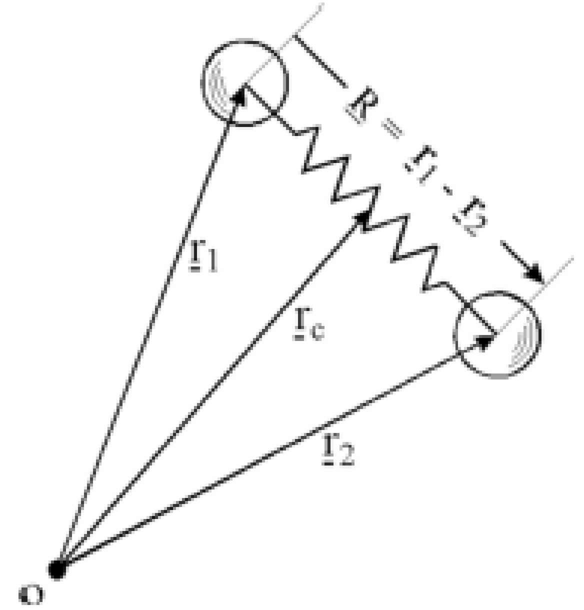


Figure 7.1-1 Representation of a dumbbell: beads 1 and 2 are connected by a spring.

Relation between the connector force and the stress tensor

$$\pi_{ij}(\underline{r}, t) = \pi_{ij}^{p}(\underline{r}, t) + \pi_{ij}^{s}(\underline{r}, t) \qquad (7.1\text{-}2)$$

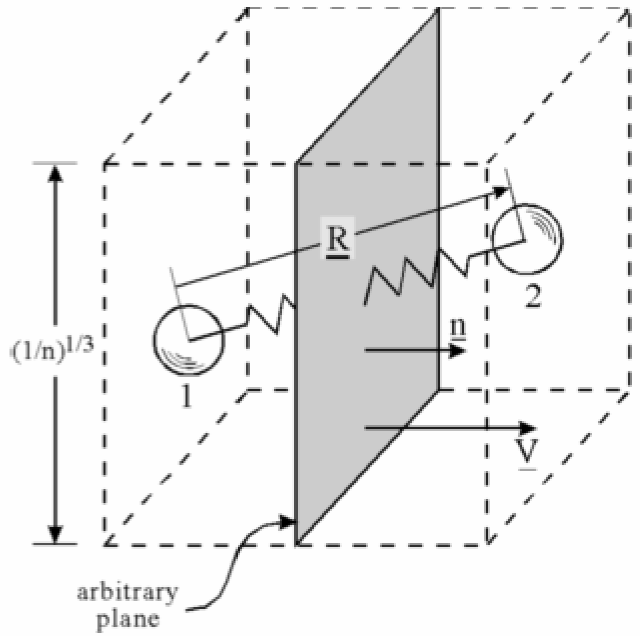


Figure 7.1-2 Dumbbell intersecting an arbitrary plane in cubic fluid volume equal to $1/n$.

The probability of any dumbbell to cross a plane of area is:

$$\frac{\underline{n} \cdot \underline{R}}{(1/n)^{1/3}} = \frac{projection\ of\ \underline{R}\ on\ \underline{n}}{length\ of\ one\ side} \qquad (7.1\text{-}3)$$

where $\underline{n}$ is the unit vector normal to the plane. The force per unit surface on the right side of the plane is given by:

$$\underline{F} = -\frac{n^{1/3}\left(\underline{n} \cdot \underline{R}\right)\underline{F}^{c}}{\left(\frac{1}{n}\right)^{2/3}} \qquad (7.1\text{-}4)$$

or in component form:

$$F_i = -n\, n_j\, R_j\, F_i^{c} \qquad (7.1\text{-}5)$$

Any force is related to the stress tensor by

$$F_i = n_j\, \pi_{ji} \qquad (7.1\text{-}6)$$

Hence, from equations 7.1-5 and 6, we obtain:

$$\pi_{ji}^{c} = -n\, R_j\, F_i^{c} \qquad (7.1\text{-}7)$$

The contribution of the beads to the total stress tensor is obtained by noting that the number of beads (1) that cross the arbitrary plane per unit surface and per unit time is:

$$n\left(\underline{\dot{r}}_1 - \underline{V}\right) \cdot \underline{n}$$

Momentum flux due to beads (1) is expressed by:

$$Q_i^{(1)} = n\, m_1 \left(\dot{r}_{1j} - V_j\right) n_j \left(\dot{r}_{1i} - V_i\right) \qquad (7.1\text{-}8)$$

Similarly for beads (2):

$$Q_i^{(2)} = n\, m_2 \left(\dot{r}_{2j} - V_j\right) n_j \left(\dot{r}_{2i} - V_i\right) \qquad (7.1\text{-}9)$$

The momentum transferred is the sum $\underline{Q} = \underline{Q}^{(1)} + \underline{Q}^{(2)}$ and:

$$Q_i = n_j\, \pi_{ij}^{b} \qquad (7.1\text{-}10)$$

$(for\ m_1 = m_2 = m)$

$$n\,m\left[\left(\dot{r}_{1i} - V_i\right)\left(\dot{r}_{1j} - V_j\right) + \left(\dot{r}_{2i} - V_i\right)\left(\dot{r}_{2j} - V_j\right)\right] \qquad (7.1\text{-}11)$$

Distribution function

$$\int\!\!\int\!\!\int\!\!\int f\left(\underline{r}_1, \dot{\underline{r}}_1, \underline{r}_2, \dot{\underline{r}}_2, t\right) d\underline{r}_1\, d\underline{r}_2\, d\dot{\underline{r}}_1\, d\dot{\underline{r}}_2 = n$$

represents the number of dumbbells per unit volume at time t for which bead (1) is in the range $d\underline{r}_1$ about $\underline{r}_1$ and at velocity in the range $d\dot{\underline{r}}_1$ about $\dot{\underline{r}}_1$.

We make the **following assumptions:**

i) We assume that the spatial and velocity distributions can be separated as follows:

$$f(\underline{r}_1, \underline{r}_2, \dot{\underline{r}}_1, \dot{\underline{r}}_2, t) = \phi(\underline{r}_1, \underline{r}_2, t)\,\Theta(\dot{\underline{r}}_1, \dot{\underline{r}}_2)$$

with

$$\iint \Theta(\dot{\underline{r}}_1, \dot{\underline{r}}_2)\, d\dot{\underline{r}}_1\, d\dot{\underline{r}}_2 = 1 \qquad (7.1\text{-}14)$$

ϕ is the distribution in the configuration space and f is the distribution in the phase space.

ii) The distribution function for the velocity is assumed to be Maxwellian. That is:

$$\Theta(\dot{\underline{r}}_1, \dot{\underline{r}}_2) = \frac{\exp\left[-\frac{m}{2}\frac{|\dot{\underline{r}}_1 - \underline{V}|^2}{k_B T} - \frac{m}{2}\frac{|\dot{\underline{r}}_2 - \underline{V}|^2}{k_B T}\right]}{\iint \exp\left[-\frac{m}{2}\frac{|\dot{\underline{r}}_1 - \underline{V}|^2}{k_B T} - \frac{m}{2}\frac{|\dot{\underline{r}}_2 - \underline{V}|^2}{k_B T}\right] d\dot{\underline{r}}_1\, d\dot{\underline{r}}_2}$$

iii) We assume that the dumbbells are distributed homogeneously and thus $\phi\ (\underline{r}_1, \underline{r}_2, t)$ depends only on the vector $\underline{R} = \underline{r}_2 - \underline{r}_1$

$$\phi\left(\underline{r}_1, \underline{r}_2, t\right) = n\ \psi\left(\underline{R}, t\right) \qquad (7.1\text{-}16)$$

In order to satisfy 7.1-12 we require that:

$$\int \psi\left(\underline{R}, t\right) d\underline{R} = 1 \qquad (7.1\text{-}17)$$

Total stress tensor:

$$\underline{\underline{\pi}}^{p} = \int\int\int\int \underline{\underline{\pi}}^{p_1} f\left(\underline{r}_1, \underline{r}_2, \dot{\underline{r}}_1, \dot{\underline{r}}_2, t\right) d\underline{r}_1\ d\underline{r}_2\ d\dot{\underline{r}}_1\ d\dot{\underline{r}}_2$$

where $\underline{\underline{\pi}}^{p_1} = \left(\underline{\underline{\pi}}^{c_1} + \underline{\underline{\pi}}^{b_1}\right)$ is the contribution of a typical dumbbell. Using results 7.1-7 and 7.1-11 as well as the simplifications implied by equations 7.1-13 to 7.1-17, we obtain (see Problem 7.5-1)

$$\pi_{ij}^{p} = -n < R_i\ F_j^{c} > + 2nk_B T\delta_{ij} \qquad (7.1\text{-}19)$$

where

$$< R_i\ F_j^{c} > = \int \psi\left(\underline{R}, t\right) R_i\ F_j^{c}\ d\underline{R} \qquad (7.1\text{-}20)$$

The polymer contribution

$$\pi_{ij}^{P} = P^{P}\,\delta_{ij} + \sigma_{ij}^{P} \qquad (7.2\text{-}21)$$

$$P^{P} = n k_B T \qquad (7.1\text{-}22)$$

Total equilibrium pressure:

$$P = P^{s} + n k_B T \qquad (7.1\text{-}23)$$

Combining equations 7.1-19, 7.1-21 and 7.1-22,

$$\sigma_{ij}^{P} = -n \langle R_i F_j^{\,c} \rangle + n k_B T \delta_{ij} \qquad (7.1\text{-}24)$$

Adding the solvent contribution:

$$\sigma_{ij} = -\eta_s\,\dot{\gamma}_{ij} - n \langle R_i F_j^{\,c} \rangle + n k_B T \delta_{ij} \qquad (7.1\text{-}25)$$

This is the **Kramers expression!**

Distribution function $\psi(\underline{R}, t)$

The principle of conservation of dumbbells:

$$\frac{\partial \psi}{\partial t}(\underline{R}, t) = -\nabla \cdot \psi(\underline{R}, t)\underline{V} \qquad (7.1\text{-}26a)$$

$$\frac{\partial \psi}{\partial t}(\underline{R}, t) = -\frac{\partial}{\partial R_i}\left(\dot{R}_i\, \psi\,(\underline{R}, t)\right) \qquad (7.1\text{-}26b)$$

Force balance on dumbbells

$$m\ddot{\underline{r}}_1 = \underline{F}_1^{\,d} + \underline{F}_1^{\,c} + \underline{F}_1^{\,b} \qquad (7.1\text{-}27a)$$

$$m\ddot{\underline{r}}_2 = \underline{F}_2^{\,d} + \underline{F}_2^{\,c} + \underline{F}_2^{\,b} \qquad (7.1\text{-}27b)$$

Stokes' law:

$$\underline{F}_1^{\,d} = -\zeta(\,\dot{\underline{r}}_1 - \underline{V}_1) \qquad (7.1\text{-}28a)$$

$$\underline{F}_2^{\,d} = -\zeta(\,\dot{\underline{r}}_2 - \underline{V}_2) \qquad (7.1\text{-}28b)$$

$$V_{1i}\,(\underline{r}_1, t) = V_i\,(\underline{r}_c, t) + \kappa_{ij}\,(\underline{r}_c, t)\,(r_{1j} - r_{cj}) \qquad (7.1\text{-}29a)$$

$$V_{2i}\,(\underline{r}_2, t) = V_i\,(\underline{r}_c, t) + \kappa_{ij}\,(\underline{r}_c, t)\,(r_{2j} - r_{cj}) \qquad (7.1\text{-}29b)$$

$$\kappa_{ij}\,(\underline{r}_c, t) = \frac{\partial}{\partial r_j} V_i\,(\underline{r}_c, t) \qquad (7.1\text{-}30)$$

Brownian forces

$$\underline{F}_1^{\,b} = -k_B T \frac{\partial}{\partial \underline{r}_1} \ln \psi\,(\underline{R}, t) \qquad (7.1\text{-}31a)$$

$$\underline{F}_2^{\,b} = -k_B T \frac{\partial}{\partial \underline{r}_2} \ln \psi\,(\underline{R}, t) \qquad (7.1\text{-}31b)$$

We neglect inertia:

$$\underline{F}^{e} = \underline{F}_2^{e} - \underline{F}_1^{e} = H\underline{R} = \zeta\,(\dot{\underline{r}}_2 - \underline{V}_2) - \zeta\,(\dot{\underline{r}}_1 - \underline{V}_1)$$

$$+ k_B T \frac{\partial}{\partial \underline{r}_2} \ln \psi - k_B T \frac{\partial}{\partial \underline{r}_1} \ln \psi$$

Change of variables

$$(\underline{r}_1, \underline{r}_2) \rightarrow (\underline{r}_c, \underline{R})$$

$$\underline{r}_c = \frac{1}{2}(\underline{r}_1 + \underline{r}_2)$$

$$\underline{R} = \underline{r}_2 - \underline{r}_1$$

Affine deformation, $\dot{\underline{r}}_{ci} = \underline{V}_i$.

$$\dot{R}_i = \kappa_{ij} R_j - \frac{2}{\zeta}\left(k_B T \frac{\partial}{\partial R_i} \ln \psi\,(\underline{R}, t) + H R_i\right) \qquad (7.1\text{-}35a)$$

$$= \kappa_{ij} R_j - \frac{2}{\zeta}\left(F_i^{\,b} + F_i^{\,c}\right) \qquad (7.1\text{-}35b)$$

$$\frac{\partial \psi}{\partial t}(\underline{R}, t) = -\frac{\partial}{\partial R_i}\left(\dot{R}_i \, \psi(\underline{R}, t)\right) \qquad (7.1\text{-}26b)$$

$$\frac{\partial \psi(\underline{R}, t)}{\partial t} = -\frac{\partial}{\partial R_i}\left[\left(\kappa_{ij} R_j - \frac{2}{\zeta}\left(F_i^{\,b} + F_i^{\,c}\right)\right) \psi(\underline{R}, t)\right] \qquad (7.1\text{-}36)$$

Integrating with R_iR_j

$$\underbrace{\int \frac{\partial}{\partial t} \psi(\underline{R}, t) R_i R_j \, d\underline{R}}_{(a)} = \underbrace{-\int R_i R_j \frac{\partial}{\partial R_k}\left(\kappa_{kl} R_l \, \psi(\underline{R}, t)\right) d\underline{R}}_{(b)}$$

$$\underbrace{+ \frac{2}{\zeta} k_B T \int R_i R_j \frac{\partial}{\partial R_k}\left(\frac{\partial}{\partial R_k}\left(\ln \psi(\underline{R}, t)\right) \psi(\underline{R}, t)\right) d\underline{R}}_{(c)}$$

$$\underbrace{+ \frac{2}{\zeta} \int R_i R_j \frac{\partial}{\partial R_k}\left(F_k^{\,c} \, \psi(\underline{R}, t)\right) d\underline{R}}_{(d)}$$

The integral (a) is:

$$\frac{D}{Dt}\int \psi\,(\underline{R},\,t)\,R_i\,R_j\,d\underline{R} = \frac{D}{Dt}\langle R_i\,R_j\rangle$$

$$(b) = \int (\delta_{ik}\,R_j\,R_l\,\kappa_{kl} + \delta_{jk}\,R_i\,R_l\,\kappa_{kl})\,\psi\,(\underline{R},\,t)\,d\underline{R}$$

$$= \langle R_j\,R_l\rangle\,\kappa_{il} + \langle R_i\,R_l\rangle\,\kappa_{jl}$$

$$(c) = -\frac{2}{\zeta}\,k_B T\int\left(\delta_{ik}\,R_j\,\frac{\partial}{\partial R_k}\,\psi\,(\underline{R},\,t) - \delta_{jk}\,R_i\,\frac{\partial}{\partial R_k}\,\psi\,(\underline{R},\,t)\right)d\underline{R}$$

$$= \frac{4}{\zeta}\,k_B T\,\delta_{ij}$$

$$(d) = -\frac{2}{\zeta} \int \left(\delta_{ik} R_j F_k^{\,c} + \delta_{jk} R_i F_k^{\,c} \right) \psi(\underline{R}, t)\, d\underline{R}$$

$$= -\frac{2}{\zeta} \left(\langle R_j F_i^{\,c} \rangle + \langle R_i F_j^{\,c} \rangle \right)$$

$$= -\frac{4}{\zeta} \langle R_i F_j^{\,c} \rangle$$

$$\frac{D}{Dt} \langle R_i R_j \rangle = \langle R_j R_k \rangle \kappa_{ik} + \langle R_i R_k \rangle \kappa_{jk} - \frac{4}{\zeta} \langle R_i F_j^{\,c} \rangle + \frac{4}{\zeta} k_B T \delta_{ij} \tag{7.1-39}$$

$$\frac{\delta}{\delta t} \langle R_i R_j \rangle = -\frac{4}{\zeta} \langle R_i F_j^{\,c} \rangle + \frac{4}{\zeta} k_B T \delta_{ij} \tag{7.1-40}$$

$$\frac{\delta}{\delta t}<R_i\,R_j> = -\frac{4}{\zeta}<R_i\,F_j^{\,c}> + \frac{4}{\zeta}k_BT\,\delta_{ij} \qquad (7.1\text{-}40)$$

Comparing with equation 7.1-24: $\sigma_{ij}^{p} = -n<R_iF_j^{\,c}> + nk_BT\delta_{ij}$

$$\sigma_{ij}^{p} = \frac{n\zeta}{4}\frac{\delta}{\delta t}<R_i\,R_j> \qquad (7.1\text{-}41)$$

Giesekus (1966) equation.

For a Hookean dumbbell , $F_i^{\,c} = H_0R_i$ Equation 7.1-24 reduces to:

$$<R_i\,R_j> = -\frac{\sigma_{ij}^{p}}{nH_0} + \frac{k_BT}{H_0}\delta_{ij} \qquad (7.1\text{-}42)$$

Combining this result with the Giesekus equation 7.1-41:

$$\sigma_{ij} + \frac{\zeta}{4H_0}\frac{\delta}{\delta t}\sigma_{ij} = -\left(nk_BT\frac{\zeta}{4H_0} + \eta_s\right)\dot{\gamma}_{ij} \qquad (7.1\text{-}43)$$

$$\sigma_{ij} + \frac{\zeta}{4H_0}\frac{\delta}{\delta t}\sigma_{ij} = -\left(nk_BT\frac{\zeta}{4H_0} + \eta_s\right)\dot{\gamma}_{ij} \quad (7.1\text{-}43)$$

This is identical to the upper convected Maxwell model with

$$\lambda_0 = \frac{\zeta}{4H_0} \quad (7.1\text{-}44)$$

and

$$\eta_0 = \frac{nk_BT\,\zeta}{4H_0} + \eta_s \quad (7.1\text{-}45)$$

7.1-2 FENE (finitely extensible nonlinear elastic) dumbbell

$$\underline{F}^c = \frac{H_0 \underline{R}}{1 - \dfrac{R^2}{R_\infty^{\ 2}}} \qquad (7.1\text{-}46)$$

FENE-P dumbbell model

$$\underline{F}^{\,c} = \frac{H_0 \underline{R}}{\left[1 - \langle R^2/R_\infty^2 \rangle\right]} \qquad (7.1\text{-}47a)$$

where $\langle R^2/R_\infty^2 \rangle$ is the average defined earlier as:

$$\langle R^2/R_\infty^2 \rangle = \int \psi(\underline{R}, t)\,(R^2/R_\infty^2)\, d\underline{R} \qquad (7.1\text{-}47b)$$

$$\langle R^2/R_\infty^2 \rangle = 1 - \frac{1}{Z(tr\underline{\underline{\sigma}}^P)} \qquad (7.1\text{-}48a)$$

$$Z(tr\underline{\underline{\sigma}}^P) = 1 + \frac{3}{b}\left[1 - \frac{tr\underline{\underline{\sigma}}^P}{3nk_BT}\right] \qquad (7.1\text{-}48b)$$

$$b = \frac{2H_0R_\infty^2}{k_BT} \qquad (7.1\text{-}48c)$$

It follows that:

$$\underline{F}^c = H_0 Z \underline{R} \qquad (7.1\text{-}49)$$

$$\sigma_{ij}^p = -nH_0Z \langle R_iR_j\rangle + nk_BT\,\delta_{ij} \qquad (7.1\text{-}50)$$

Taking the upper convected derivative and combining with Giesekus equation 7.1-41

$$\sigma_{ij}^p = \frac{n\zeta}{4}\frac{\delta}{\delta t}\langle R_i R_j\rangle \qquad (7.1\text{-}41)$$

$$Z\sigma_{ij}^p + \lambda_H \frac{\delta \sigma_{ij}^p}{\delta t} - \lambda_H\left(\sigma_{ij}^p - nk_BT\delta_{ij}\right)\frac{D}{Dt}\ln Z = -nk_BT\,\lambda_H\dot{\gamma}_{ij}$$

Example 7.1-1 Steady shear functions for the FENE-P model

Solution

For steady shear flow, $V_1 = \dot{\gamma} x_2$, $V_2 = V_3 = 0$.

$$Z\begin{bmatrix} \sigma^p_{11} & \sigma^p_{12} & \sigma^p_{13} \\ \sigma^p_{21} & \sigma^p_{22} & \sigma^p_{23} \\ \sigma^p_{31} & \sigma^p_{32} & \sigma^p_{33} \end{bmatrix} - \lambda_H \dot{\gamma} \begin{bmatrix} 2\sigma^p_{21} & \sigma^p_{22} & \sigma^p_{23} \\ \sigma^p_{22} & 0 & 0 \\ \sigma^p_{23} & 0 & 0 \end{bmatrix} = -n k_B T \lambda_H \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$Z\sigma^p_{11} - 2\lambda_H \dot{\gamma} \sigma^p_{21} = 0$$

$$Z\sigma^p_{21} - \lambda_H \dot{\gamma} \sigma^p_{22} = -n k_B T \lambda_H \dot{\gamma}$$

$$Z\sigma^p_{22} = 0$$

$$Z\sigma^p_{23} = Z\sigma^p_{32} = 0 \qquad (7.1\text{-}53)$$

$$Z\sigma^p_{31} - \lambda_H \dot{\gamma} \sigma^p_{23} = 0$$

$$Z\sigma^p_{33} = 0$$

Simplifying:

$$Z\sigma_{21}^{p} = -nk_BT\lambda_H\dot{\gamma} \tag{7.1-54a}$$

$$Z\sigma_{11}^{p} = 2\lambda_H\sigma_{21}^{p}\dot{\gamma} \tag{7.1-54b}$$

and equation 7.1-48b reduces to:

$$Z = 1 + \frac{3}{b}\left[1 - \frac{\sigma_{11}^{p}}{3nk_BT}\right] \tag{7.1-55}$$

For $\dot{\gamma} \to 0$, $\sigma_{11}^{p} \to 0$, $Z \to 1 + 3/b$. Hence:

$$\sigma_{21}^{p} = -\frac{nk_BT\lambda_H\dot{\gamma}}{1 + 3/b} = -(\eta_0 - \eta_s)\dot{\gamma} \tag{7.1-56}$$

$$\eta_0 - \eta_s = \frac{nk_BT\lambda_H b}{b + 3} \tag{7.1-57}$$

Dimensionless variables:

$$\xi = \frac{\sigma_{11}^{p}}{3nk_BT} \quad (7.1\text{-}58a)$$

$$\nu = \frac{\sigma_{21}^{p}}{3nk_BT} \quad (7.1\text{-}58b)$$

Equations 7.1-54 reduce to:

$$\left[1 + \frac{3}{b}(1 - \xi)\right]\nu = -\frac{1}{3}\lambda_H\dot{\gamma} \quad (7.1\text{-}59a)$$

$$\left[1 + \frac{3}{b}(1 - \xi)\right]\xi = 2\lambda_H\dot{\gamma}\,\nu \quad (7.1\text{-}59b)$$

We get,

$$-\xi = 6\nu^2 \quad (7.1\text{-}60a)$$

and

$$\nu^3 + \frac{1}{6}\left[(1 + b/3)\right]\nu + \frac{b}{54}(\lambda_H\dot{\gamma}) = 0 \quad (7.1\text{-}60b)$$

The real solution of equation 7.1-60b is:

$$\nu = \left(-C_1 + C_2\right)^{1/3} + \left(-C_1 - C_2\right)^{1/3} \qquad (7.1\text{-}61a)$$

where

$$C_1 = \frac{b}{108}\left(\lambda_H \dot{\gamma}\right) \qquad (7.1\text{-}61b)$$

$$C_2 = \left(C_1^2 + \left(\frac{3 + b}{54}\right)^3\right)^{1/2} \qquad (7.1\text{-}61c)$$

From equation 7.1-60a:

$$\Psi_1 = -\frac{\left(\sigma_{11}^p - \sigma_{22}^p\right)}{\dot{\gamma}^2} = \frac{2(\eta - \eta_s)^2}{nk_BT} \qquad (7.1\text{-}62)$$

For $\dot{\gamma} \to \infty$, from equation 7.1-60b:

$$\nu^3 + \frac{1}{6}\left[\left(1 + b/3\right)\right]\nu + \frac{b}{54}\left(\lambda_H \dot{\gamma}\right) = 0$$

$$\nu = \frac{\sigma_{21}^p}{3nk_BT} = \left|\frac{b}{54}\lambda_H \dot{\gamma}\right|^{1/3} \qquad (7.1\text{-}63)$$

Hence, FENE-P model predicts in simple shear flow:

$$\eta - \eta_s \propto \left|\lambda_H \dot{\gamma}\right|^{-2/3} \qquad (7.1\text{-}64)$$

$$\Psi_1 \propto \left|\lambda_H \dot{\gamma}\right|^{-4/3} \qquad (7.1\text{-}65)$$

$$\Psi_2 = 0$$

7.1-3 Rouse and Zimm models

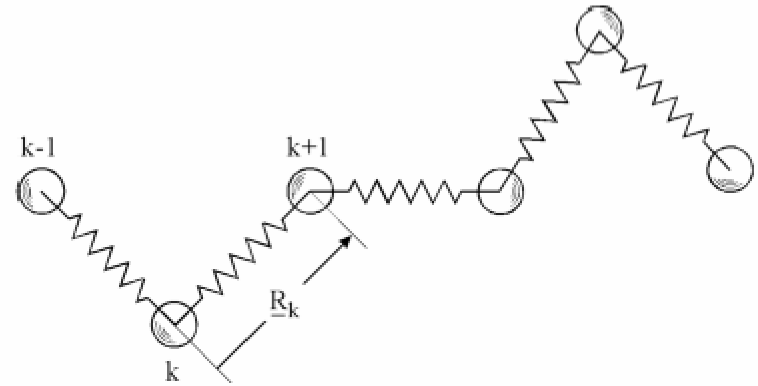


Figure 7.1-3 *N* beads connected by $N-1$ springs.

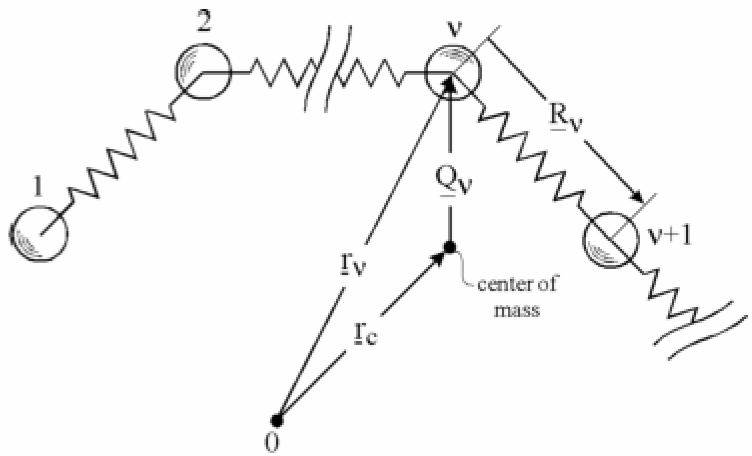


Figure 7.1-4 Bead spring model, identifying the position vectors.

Constitutive equation:

$$\sigma_{ij} = -\eta_s \dot{\gamma}_{ij} - \int_{-\infty}^{t} n k_B T \sum_k \frac{e^{-(t-t')/\lambda_k}}{\lambda_k} \Gamma_{ij}^{-1}(t') dt' \qquad (7.1\text{-}92)$$

with the relaxation times given (for the Rouse model) by :

$$\lambda_k \approx \frac{\zeta/2H_0}{4(k\pi/2N)^2} = \frac{6\,(\eta_0-\eta_s)\,M}{c\pi^2\,RTk^2} \qquad (7.1\text{-}91)$$

In the Zimm model, hydrodynamic interaction is accounted for and a different expression is obtained for the relaxation times.

7.4 Conformation tensor rheological models

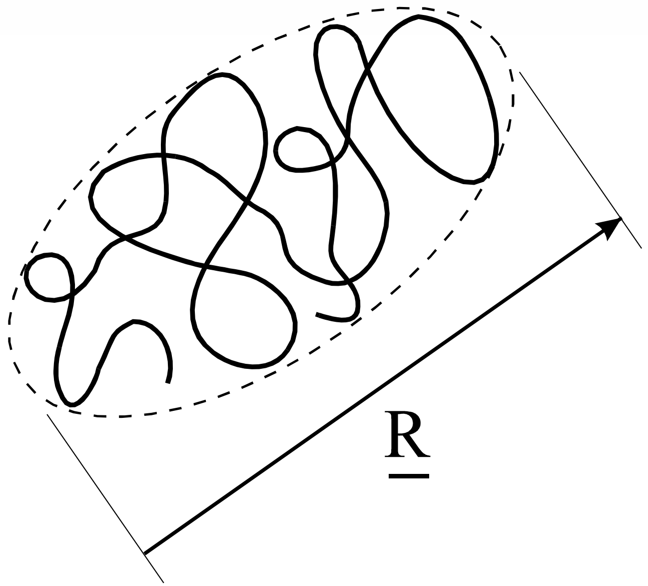
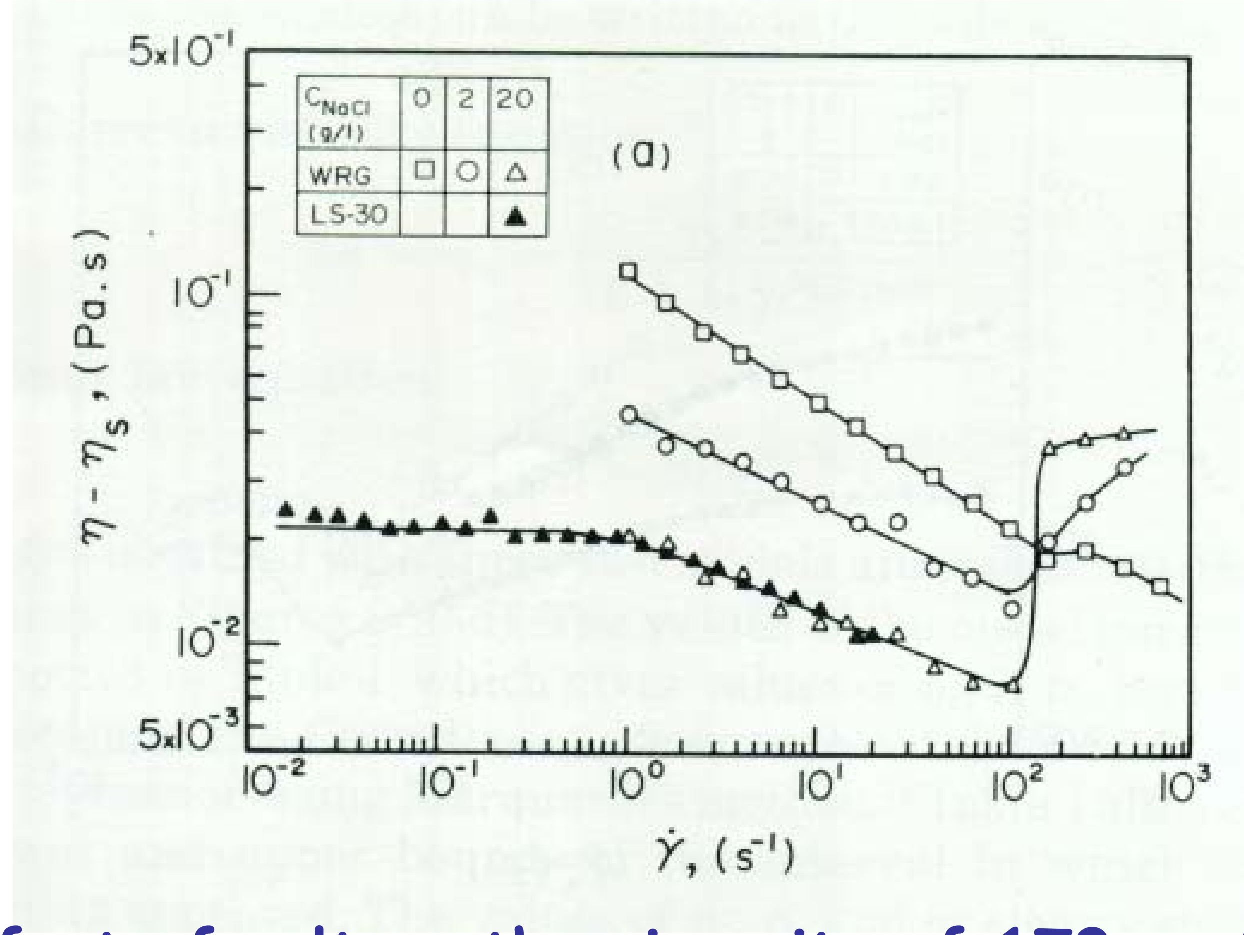


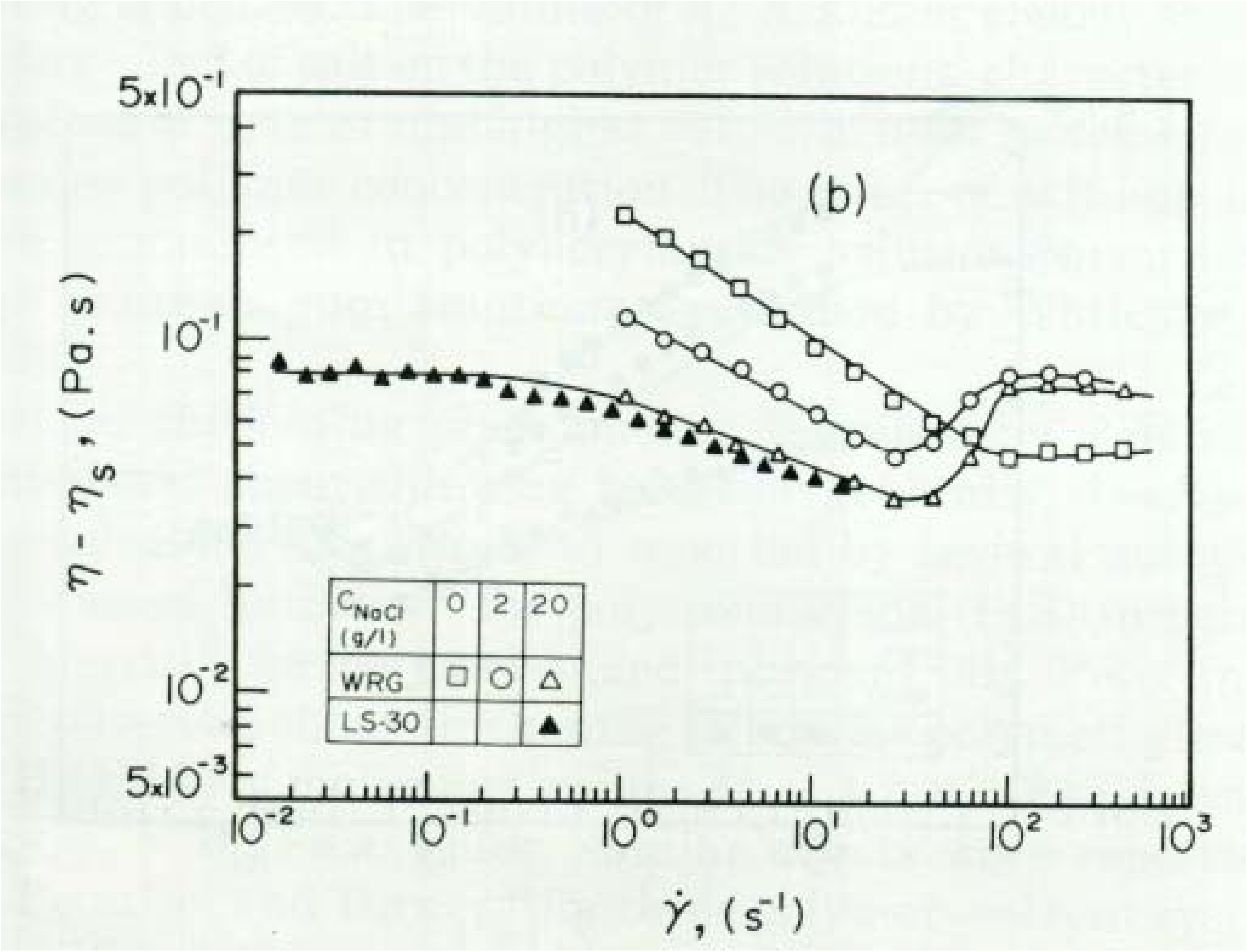
Figure 7.4-1 Polymeric chain in a coil conformation.

$$\underline{\underline{c}}\,(\underline{R},\,t) = \langle \underline{R}\,\underline{R} \rangle = \int \psi(\underline{R},\,t)\,\underline{R}\,\underline{R}\;d\,R$$

Motivation: Strain-hardening observed for dilute polyacrylamide solutions



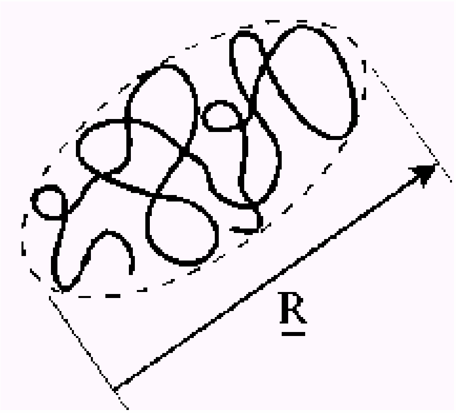
Effect of salt on the viscosity of 170 mg/L HPAM in water (Aït-Kadi et al., J. Rheol, 1987)



Effect of salt on the viscosity of 340 mg/L HPAM in water (Aït-Kadi et al., J. Rheol, 1987)

Basic description of the conformation model

$$\underline{\underline{c}}(\underline{R}, t) = \langle \underline{R}\,\underline{R} \rangle = \int \psi(\underline{R}, t)\,\underline{R}\,\underline{R}\,d\,\underline{R}$$



Following Grmela (1986),

$$\frac{D}{Dt}\underline{\underline{c}}(t) = \frac{1}{2}(2-\xi)\left[\underline{\underline{\kappa}}\cdot\underline{\underline{c}} + \underline{\underline{c}}\cdot\underline{\underline{\kappa}}^{+}\right] - \frac{\xi}{2}\left[\underline{\underline{\kappa}}^{+}\cdot\underline{\underline{c}} + \underline{\underline{c}}\cdot\underline{\underline{\kappa}}\right] - \underline{\underline{\Lambda}}(\underline{\underline{c}})\cdot\underline{\underline{c}}\cdot\frac{dA(\underline{\underline{c}})}{d\,\underline{\underline{c}}}$$

κ transpose of the velocity gradient tensor

$A(\underline{\underline{c}})$ contribution to the Helmholtz free energy functional

$\underline{\underline{\Lambda}}(\underline{\underline{c}})$ mobility tensor

ξ slip parameter

Expression for the stress

$$\underline{\underline{\sigma}}^{p} = -2n(1-\xi)\,\frac{dA(\underline{\underline{c}})}{d\,\underline{\underline{c}}}\cdot\underline{\underline{c}}$$

7.4-2 FENE-Charged Macromolecules

$$A(\underline{\underline{c}}) = -H_0\, R_\infty^2 \ln\left(1 - tr\underline{\underline{c}} / R_\infty^2\right) + E\, tr(\underline{\underline{c}})^{-1/2} - \frac{k_B}{2} T \ln \det \underline{\underline{c}}$$

FENE-P potential

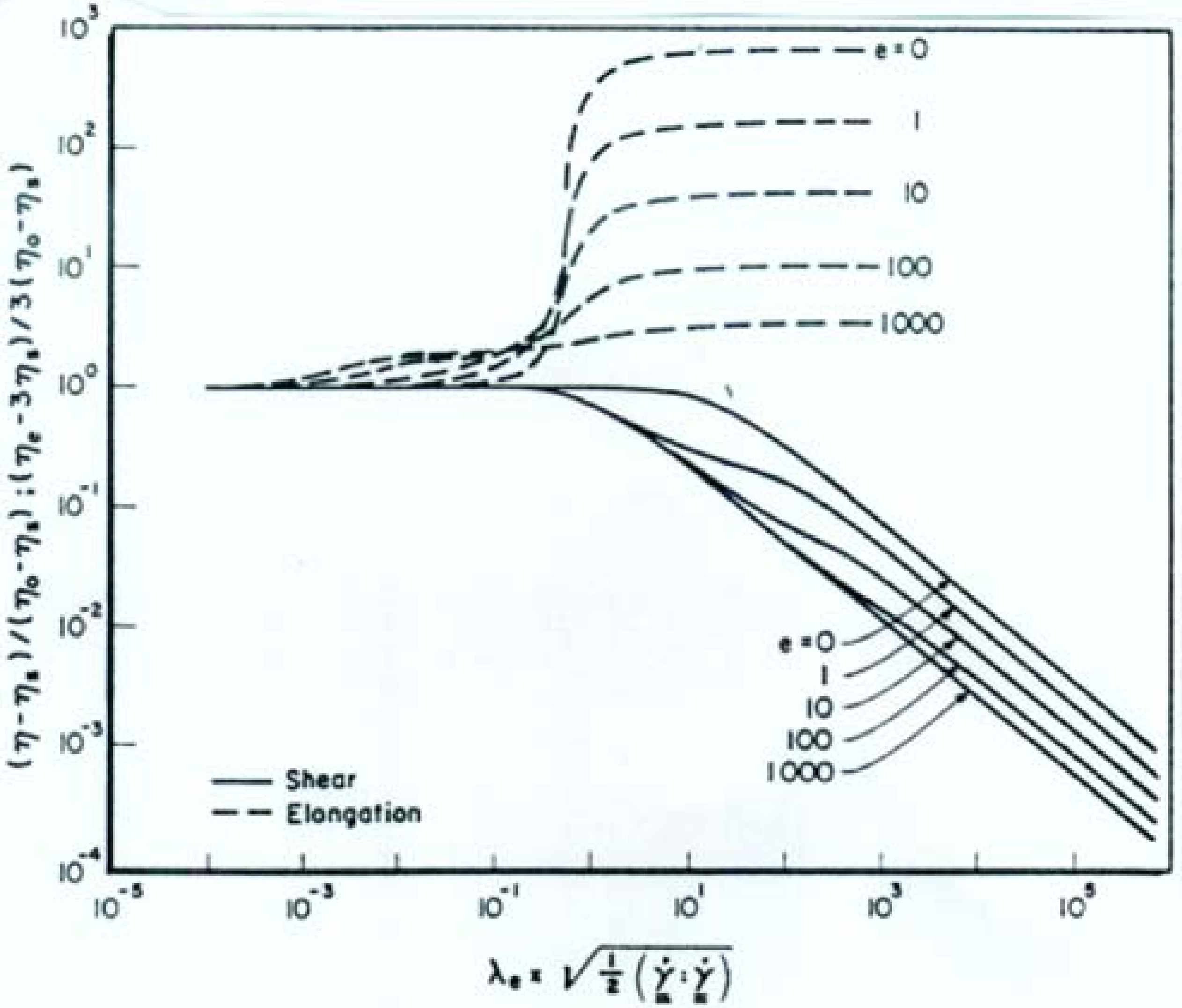
Coulombic potential

Brownian motion

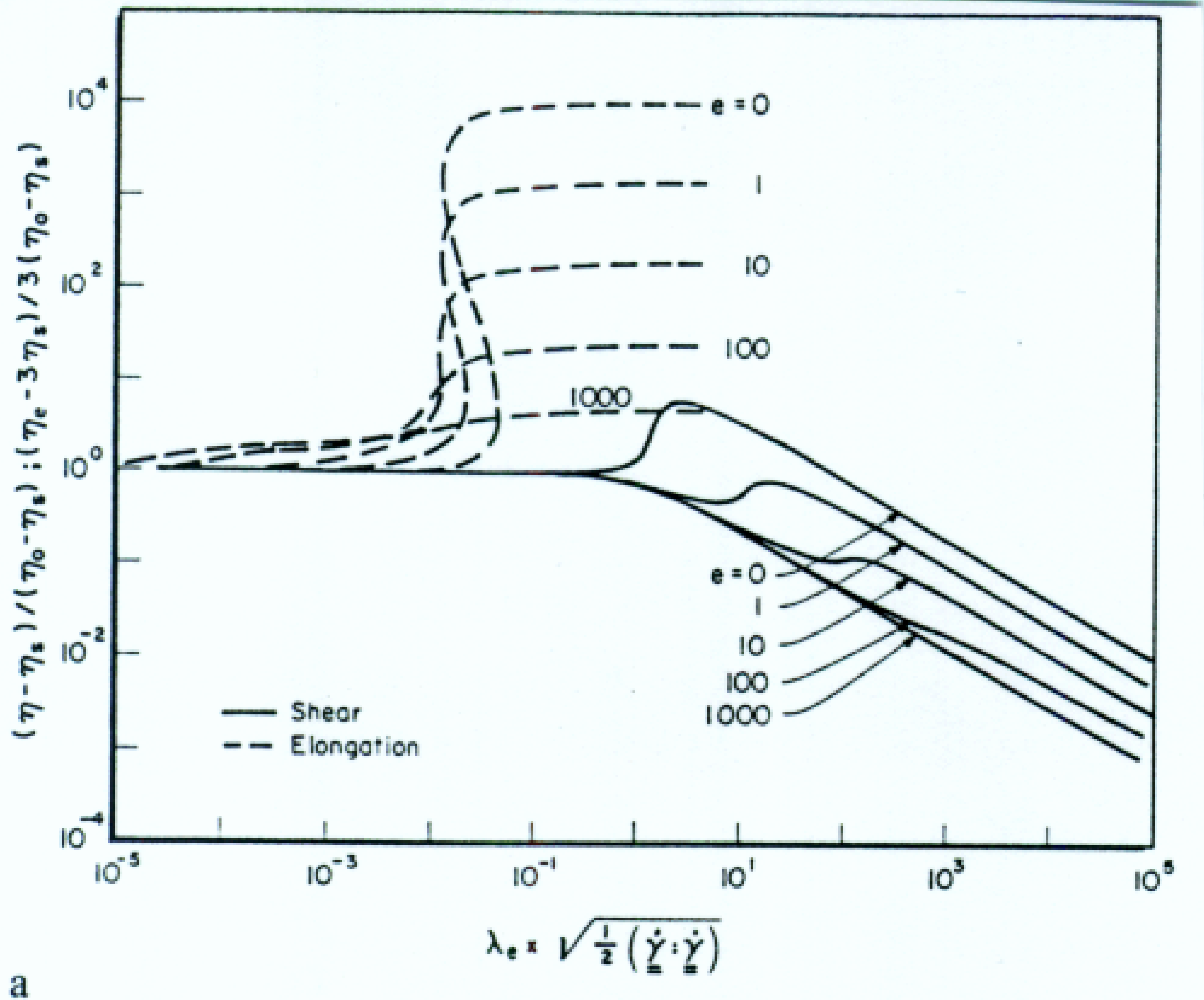
The mobility is taken to be a function of the deformation:

$$\Lambda(tr\underline{\underline{c}}) = \Lambda_0 / (1 + \beta\chi)$$

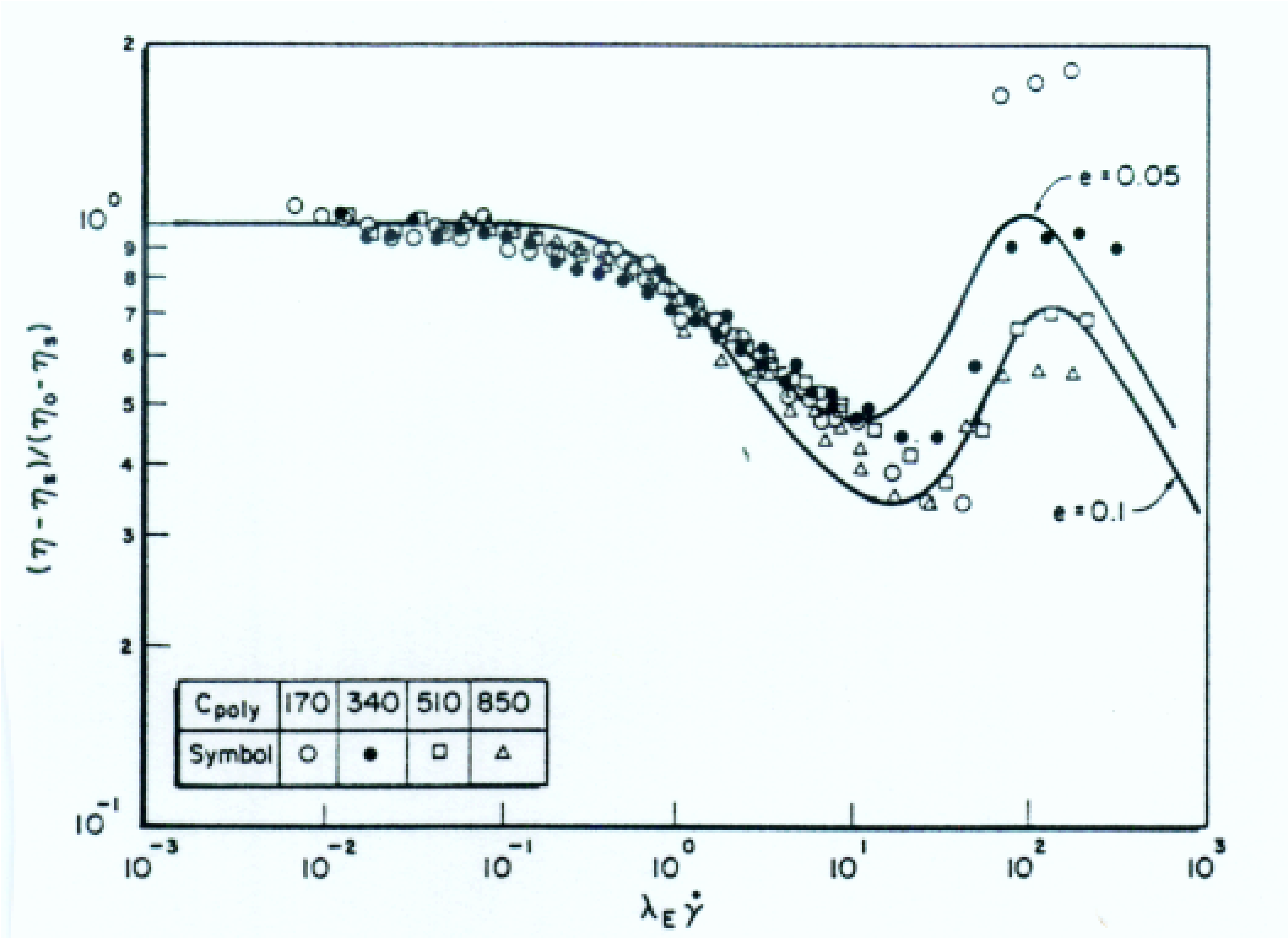
where $\chi \left(= \sqrt{tr\underline{\underline{c}} / R_\infty^2}\right)$ → reduced extension



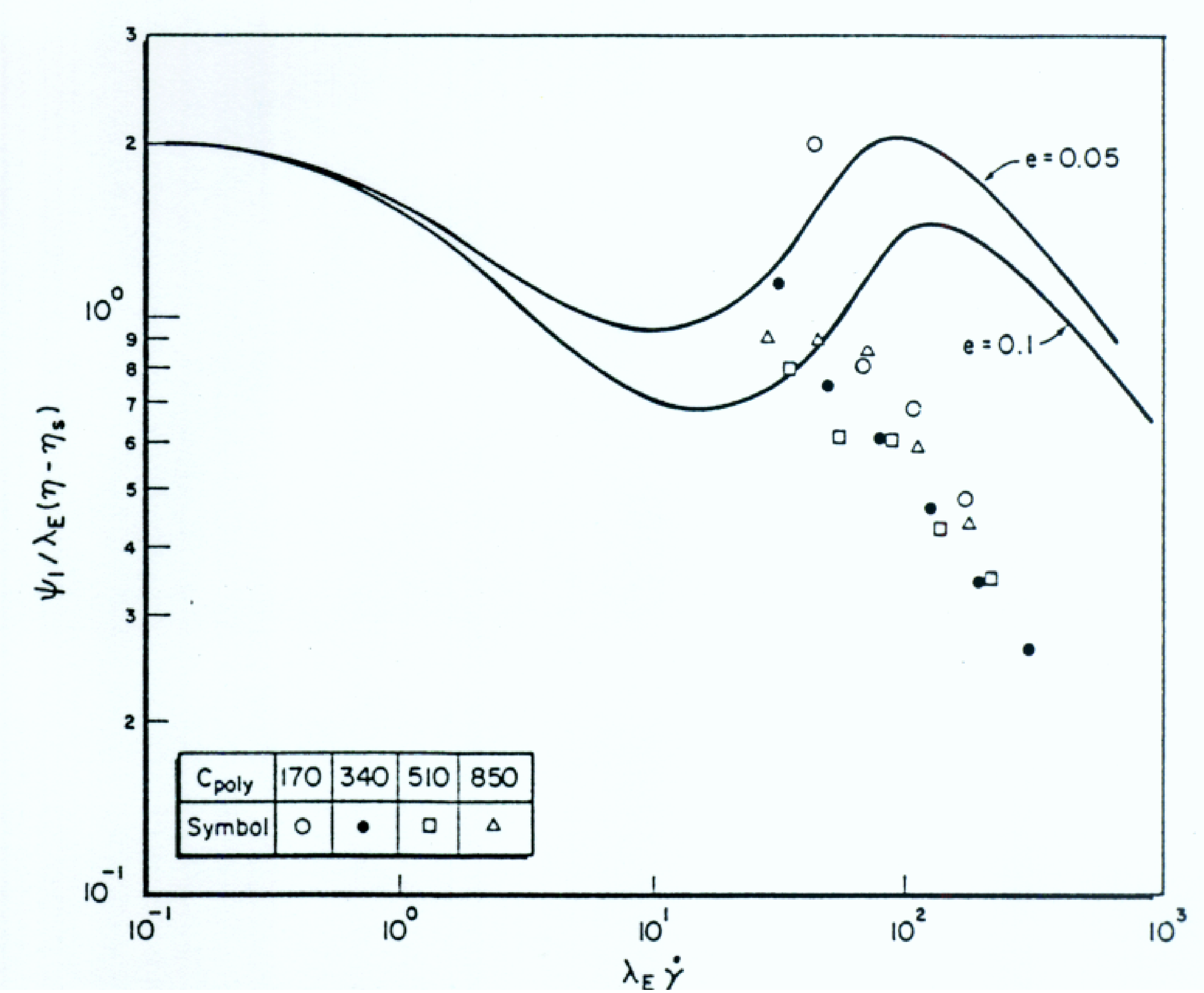
Effect of the electrostatic parameter *e* on the steady shear and elongation reduced viscosity $b = 1000,\ \xi = \beta = 0$ (Adapted from Ait-Kadi et al., 1988).



Predicted shear and elongational viscosity vs. reduced shear rate for b= 1000 and β=100



Reduced shear viscosity data for PAA Pusher-700 solutions. $C_{NaCl} = 20g/L$. The model parameters are: $b = 10^5$, $\beta = 5$ and $\xi = 0$ (Adapted from Ait-Kadi et al., 1988).



Ratio of normal stress and shear stress for HPAAm solutions in presence of salt (C_{NaCl} = 20 g/L); the model parameters are b=10^5, β = 5.

7.4-3: Rod-Like and Worm-Like Macromolecules

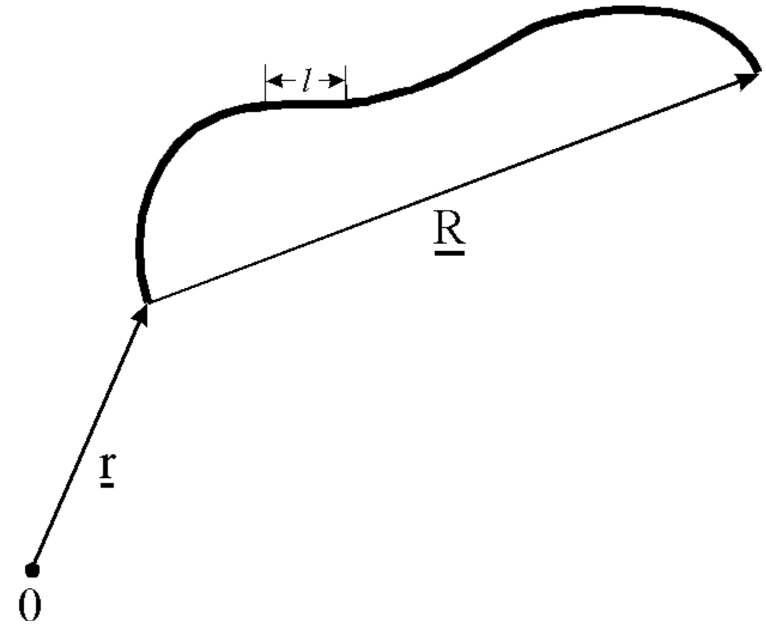


Fig. 7.4-5 Worm-like molecule

Free energy:

$$A(\underline{\underline{c}}) = U(\underline{\underline{c}}) - TS(\underline{\underline{c}}) = \frac{1}{2}k_B T\left[BF(\underline{\underline{c}}) - S_B \ln\det\frac{\underline{\underline{c}}}{R_0^2} + 2S_L tr\left(\frac{\underline{\underline{c}}}{R_0^2}\right)^{-1}\right]$$

S_L = flexibility parameter

S_B = parameter related to Brownian motion

B = Lagrange multiplier , obtained from the following constraint:

$$\frac{dF}{dt} = \frac{d}{dt}(tr\underline{\underline{c}} - R_0^2) = 0$$

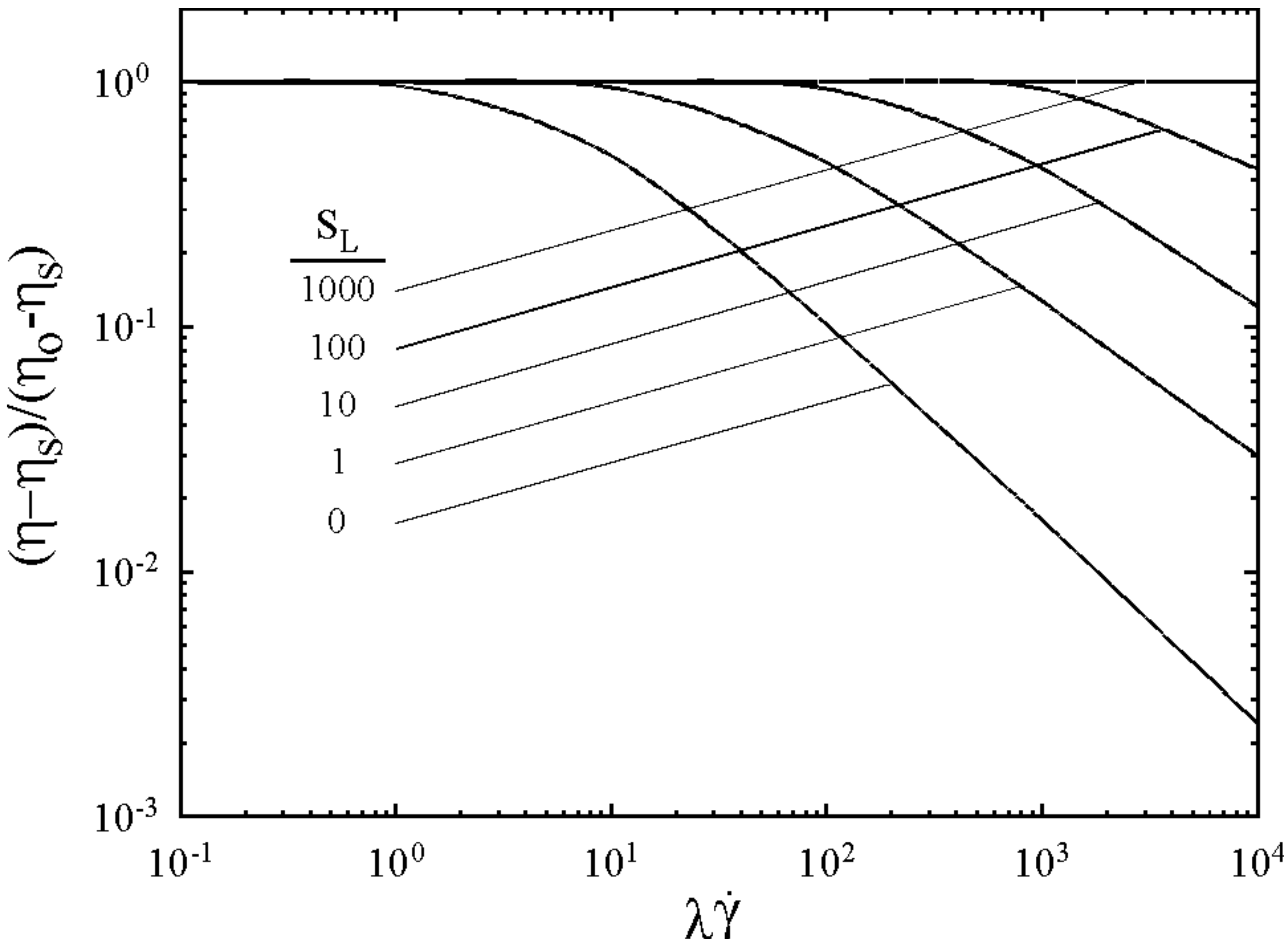


Fig. 7.4-6 Effect of chain flexibility on reduced shear viscosity

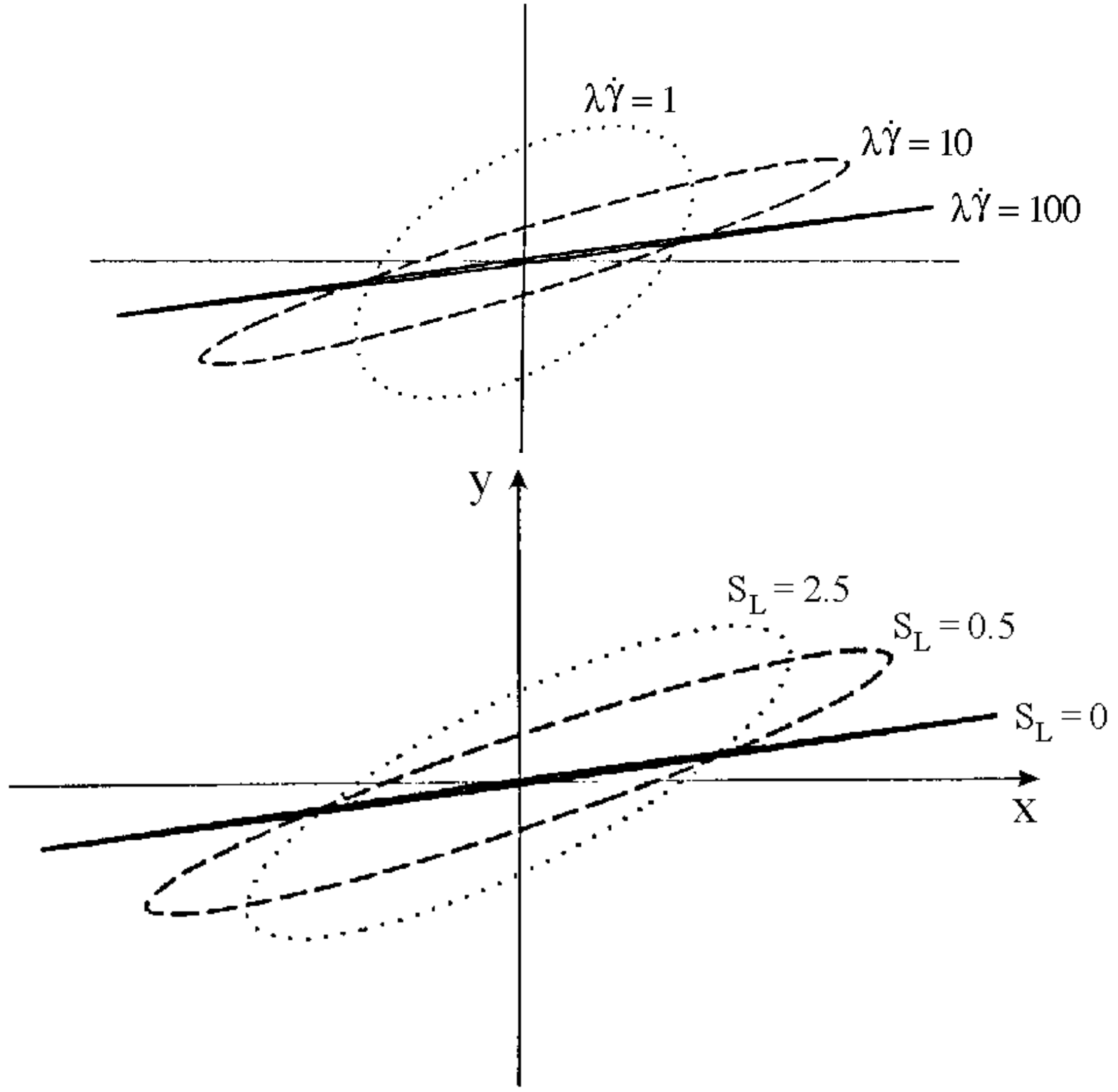


Fig. 7.4-7 Conformation tensor in simple shear flow, a) rigid rod; b) effect of chain flexibility