

# Ch 08

## Kinetic theories

# Distribution function

$$\psi_0(\mathbf{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 \exp(-\beta^2 R^2) \quad \text{Freely jointed chain at equilibrium}$$

$$S = k_B \ln(\Omega) = k_B \ln(c\psi_0) = k_B \left[ \ln c + 3 \ln(\beta / \sqrt{\pi}) - \beta^2 R^2 \right]$$

$$\mathbf{F}^s = \frac{\partial W}{\partial \mathbf{R}} = -T \frac{\partial S}{\partial \mathbf{R}} = 2k_B T \beta^2 \mathbf{R}$$

Gaussian chain acts like a Hookean spring

# Stress

$$\boldsymbol{\sigma}^p = \nu \langle \mathbf{R} \mathbf{F}^s \rangle \quad \langle \cdot \rangle \equiv \int \psi \cdot dR^3 \quad \sigma^p = 2k_B T \nu \beta^2 \langle \mathbf{R} \mathbf{R} \rangle$$

Stresses, produced by distortions of the distribution of polymer configurations

Stresses, interpreted in terms of anisotropies in molecular orientations

# Rubber elasticity theory

At equilibrium 
$$\psi_0(\mathbf{R}') = \left( \frac{\beta}{\sqrt{\pi}} \right)^3 \exp(-\beta^2 R'^2)$$

If the crosslink points deform affinely 
$$\boldsymbol{\sigma} = \nu k_B T \begin{pmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{pmatrix} = G\mathbf{B}$$

Purely elastic model, valid only at small frequency

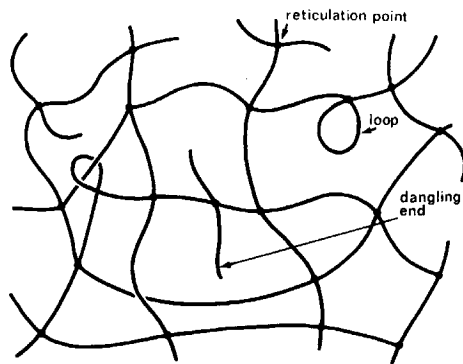


Figure 3.6 Schematic of a cross-linked polymer network. (Reprinted from Pierre-Gilles de Gennes, *Scaling Concepts in Polymer Physics*, Copyright © 1979, by Cornell University. Used by permission of the publisher, Cornell University Press.)

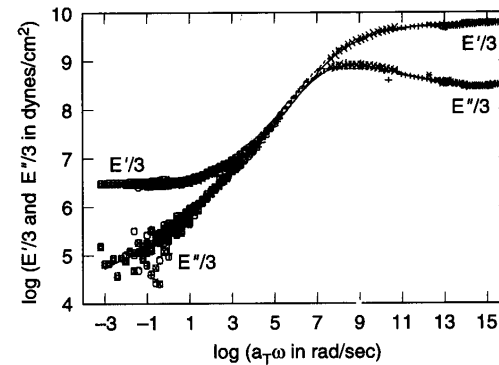


Figure 3.8 Storage and loss moduli versus reduced frequency in small-amplitude oscillatory deformation for a cross-linked polyurethane rubber, Sorbothane 70, at 20°C. The imposed deformation was uniaxial extension, yielding tensile moduli  $E'$  and  $E''$  which were converted to shear moduli using  $G' = E'/3$  and  $G'' = E''/3$ . The data at 16 different temperatures ranging from -81°C to 80°C were collapsed to a “master curve” using methods described in Section 3.5.2. (From Larson et al. 1996, reprinted with permission from Steinkopff Publishers.)

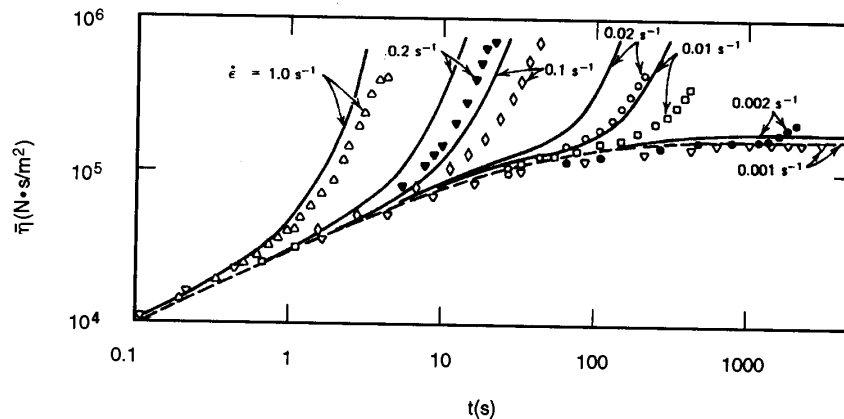
At high frequencies, the strands are not able to relax their conformations fast enough to keep up with the imposed deformation, and energy is dissipated.

# Temporary network model

Polymer chains are physically restrained by temporary junctions that spontaneously form and break (physical junction/entanglements).

$$\boldsymbol{\sigma} = \int_{-\infty}^t m(t-t') \mathbf{B}(t', t) dt' \quad m(t-t') = \sum_i \frac{G_i}{\tau_i} \exp[-(t-t')/\tau_i]$$

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad G''(\omega) = \sum_i G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$



**Figure 3.10** Predictions of the temporary network model [Eq. (3-24)] (lines) compared to experimental data (symbols) for start-up of uniaxial extension of Melt I, a long-chain branched polyethylene, using a relaxation spectrum fit to linear viscoelastic data for this melt. (From Bird et al. *Dynamics of Polymeric Liquids, Vol. 1: Fluid Mechanics*, Copyright © 1987. Reprinted by permission of John Wiley & Sons, Inc.)

Predicts:

- first normal stress difference
- stress relaxation after cessation of flow
- elastic recovery after removal of stress
- time dependent extensional viscosity

No indication of the relationship between the relaxation spectrum and the molecular relaxation processes.

# Elastic dumbbell model

## Force balance

$$\frac{1}{2} \zeta (\dot{\mathbf{R}} - \mathbf{R} \cdot \nabla \mathbf{v}) + 2k_B T \beta^2 \mathbf{R} + k_B T \frac{\partial \ln \psi}{\partial \mathbf{R}} = \mathbf{0}$$

## Smoluchowski equation

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

$$\text{Diffusion equation} \quad \frac{\partial \psi}{\partial t} + \frac{\partial}{\partial \mathbf{R}} \cdot \left[ \mathbf{R} \cdot \nabla \mathbf{v} \psi - \frac{4k_B T \beta^2}{\zeta} \mathbf{R} \psi - \frac{2k_B T}{\zeta} \frac{\partial \psi}{\partial \mathbf{R}} \right] = 0$$

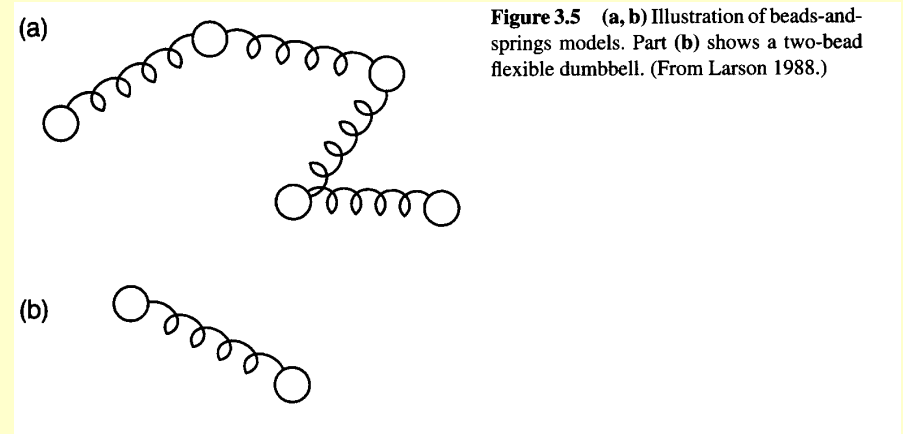
## Stress (Kramer's form)

$$\boldsymbol{\sigma}^p = 2k_B T \nu \beta^2 \langle \mathbf{R} \mathbf{R} \rangle$$

## Upper convected Maxwell model

$$\overset{\nabla}{\boldsymbol{\sigma}}^p + \frac{1}{\tau} (\boldsymbol{\sigma}^p - G \boldsymbol{\delta}) = \mathbf{0} \quad \overset{\nabla}{\mathbf{X}} \equiv \dot{\mathbf{X}} - \nabla \mathbf{v}^T \cdot \mathbf{X} - \mathbf{X} \cdot \nabla \mathbf{v} \quad G = \nu k_B T, \quad \tau = \frac{\zeta}{8k_B T \beta^2}$$

$$\text{Oldroyd-B model} \quad \boldsymbol{\sigma} = \boldsymbol{\sigma}^p + \boldsymbol{\sigma}^s$$



# Rouse model

Force balance  $\zeta_b (\dot{\mathbf{R}}_i - \mathbf{R}_i \cdot \nabla \mathbf{v}) + k_B T \sum_{j=1}^{N_s} A_{ij} \left( 2\beta_s^2 \mathbf{R}_j + \frac{\partial \ln \psi}{\partial \mathbf{R}_j} \right) = \mathbf{0}$

## Upper convected Maxwell model

$$\boldsymbol{\sigma}^P = \sum_{i=1}^{N_s} \boldsymbol{\sigma}_i \quad \nabla \cdot \boldsymbol{\sigma}_i + \frac{1}{\tau_i} (\boldsymbol{\sigma}_i - G_i \boldsymbol{\delta}) = \mathbf{0}$$

$$G_i = G = \nu k_B T, \quad \tau_i = \frac{\zeta_b}{16k_B T \beta_s^2 \sin^2(i\pi/2(N_s + 1))}$$

Predicts a nontrivial distribution of polymer relaxation times

$$\tau_i \approx \frac{\zeta_b (N_s + 1)^2}{4\pi^2 \beta_s^2 i^2 k_B T} = \frac{\tau_1}{i^2}, \quad G_i = G = \nu k_B T \quad \tau_i \approx \frac{\zeta_0 N^2 b^2}{6\pi^2 i^2 k_B T} = \frac{6(\eta - \eta_s)}{\pi^2 i^2 \nu k_B T}$$

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad G''(\omega) = \sum_i G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$

$$G' = G'' - \eta_s \omega \propto \omega^{1/2} \quad \text{at high frequencies}$$

# Time-temperature superposition

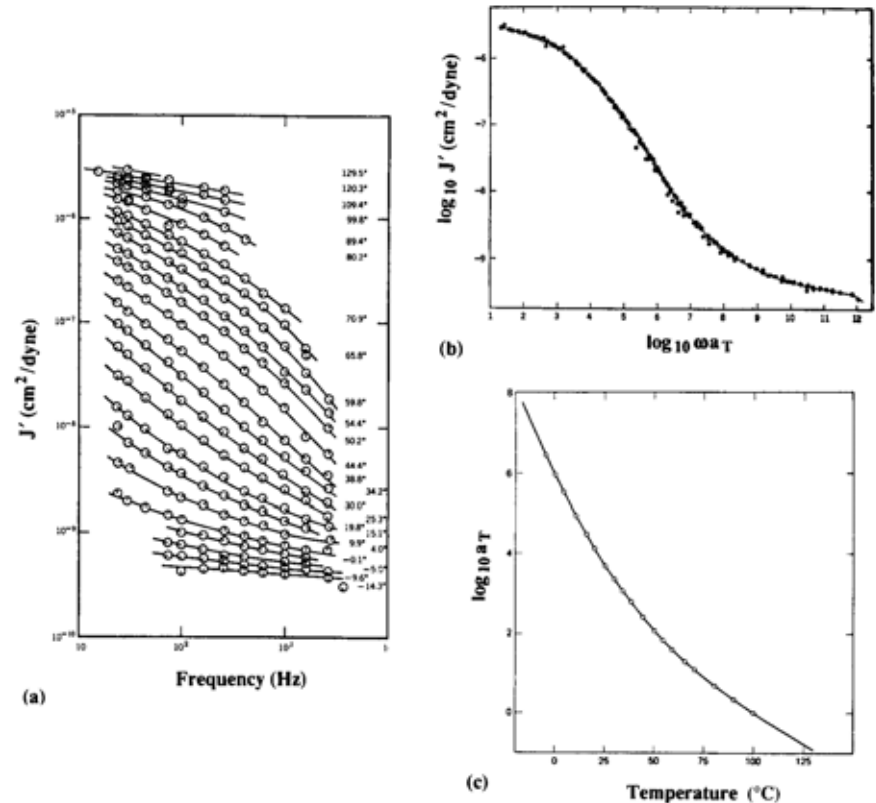
$$G'(\omega) = \sum_i G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad G''(\omega) = \sum_i G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad G_i = G = \nu k_B T, \quad \tau_i = \frac{\zeta_b}{16 k_B T \beta_s^2 \sin^2(i\pi / (2(N_s + 1)))}$$

On a log-log plot, a change in temperature merely shifts the curves along the frequency axis, without changing their shape

Shift along modulus axis is small or negligible

$$\log a^T = \frac{-c_1^0 (T - T_0)}{c_2^0 + T - T_0}$$

$$a_T = \frac{\eta_o(T)}{\eta_o(T_o)}$$



**Figure 3.12** (a) Storage compliance  $J'$  of poly(*n*-octyl methacrylate) versus frequency measured at 24 temperatures, given in degrees Celsius. (b) "Master curve" of  $J'$  versus reduced frequency  $\omega a_T$  obtained from the data of (a) by time temperature shifting. (c) Temperature-dependence of the shift factor  $a_T$  required to obtain the master curve of (b); the line is a fit of the WLF equation, (3-45a), with  $T_0 = 373.2$  K,  $c_1^0 = 7.60$ , and  $c_2^0 = 227.3$  K. (From Ferry *Viscoelastic Properties of Polymers*, Copyright © 1980. Reprinted by permission of John Wiley & Sons, Inc.)