

# MOLECULAR RHEOLOGY OF POLYMER SYSTEMS

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## ABSTRACT

Some general principles of constructing molecular theories of polymer systems are discussed. The theories based on statistical mechanics combined with simplified concepts in molecular structure comprise the following fundamental equations: equation of continuity in an  $N$ -dimensional configuration space, kinetic equations describing the motion of the structural units involved, dynamic equations, i.e. relations between the local tension and configuration characteristics, kinetic equations describing the rates of formation and dissociation of structural units in the system. Some simplified concepts in intra- and inter-molecular interactions in macromolecular systems are given. Two examples of model systems are analysed systematically; a dilute solution of flexible chain-macromolecules, and an entangled network system typical for concentrated polymer solutions and melts.

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## INTRODUCTION

The importance of molecular considerations in polymer rheology is rather obvious and hardly need be argued. The theory of mechanical (as well as any other) macroscopic characteristics of polymer systems formulated in terms of molecular structure leads to a deeper understanding of the mechanisms responsible for the observed phenomena, and enables one to predict the physical behaviour of various materials, and to design new materials with modified structure and properties. Molecular theories seem to make the best basis for physically reasonable assumptions in the derivation of constitutive equations from continuum considerations.

The term 'molecular theory' is, however, far from being unequivocal. There are in the polymer literature many treatments claimed to be, and (even worse) considered by many readers as, 'molecular theories' while based on quite arbitrary or unfounded model assumptions. So, for example, in attempts to reproduce the empirical '3.4 power law' (shear viscosity proportional to the 3.4th power of the molecular weight of polymer) Bueche<sup>1</sup> assumed some 'rigid rotations' of macromolecules in entangled systems; for the same purpose Graessley<sup>2</sup> postulated a kind of 'slalom motion' of a macromolecule through entanglement loops of other chains, while Hayashi<sup>3</sup> and Pokrovskii<sup>4</sup> assumed special forms of frictional coefficients. None of these concepts was based on systematic molecular considerations or had a clear physical significance.

Various criteria can be considered in the comparison of individual

theories. Let us discuss the following three: fundamentality, generality, and tractability.

The first criterion requires that the theory involves a minimum number of assumptions and those as close as possible to first principles. The best theoretical basis for molecular rheology is provided by statistical mechanics though, as will be shown below, introduction of some additional concepts and simplifications is unavoidable.

The generality of molecular theories should concern first of all the boundary conditions (geometry and time-régime of deformation, external fields etc.) so that a broad range of physical phenomena could be analysed. On the other hand, molecular theories cannot be too general with respect to the structures considered. They are usually rather specific and cover narrow classes of molecular models corresponding to the different structures of real systems.

Tractability of a theory requires that the results be presentable in a transparent and simple form convenient for interpretation of observed phenomena and description of technical processes. It is my feeling, however, that a really fundamental molecular theory can hardly yield results tractable enough for application in routine experimental methods and solution of technical problems. Of course, every theory should be tractable enough for physically significant conclusions to be drawn from it, but an improvement of tractability at the cost of fundamentality or generality would not be advisable for molecular theories.

The aim of the present paper is to discuss some general principles for the construction of a molecular rheological theory of polymer systems and to define the position which such theories occupy in the framework of the physical sciences. Some of the views expressed in this paper were formulated by the author (in a more crude and primitive form) two years ago<sup>5</sup>.

## STATISTICAL MECHANICS AND SIMPLIFIED MOLECULAR THEORIES

Statistical mechanics, considering individual atoms (or simple molecules) as kinetic units provides the most fundamental basis for any molecular theory. The positions  $\mathbf{q}$  and momenta  $\mathbf{p}$  of the atoms considered form the set of configuration variables, and the interatomic potentials  $U$  lead to the interaction forces and 'local' stress dyadics  $\sigma_{loc}$ . The local stress averaged over the entire ensemble of kinetic units yields the average (= macroscopic) stress tensor  $\sigma$ . Such an approach has been successfully applied to the molecular theory of monatomic fluids<sup>6,7</sup>. The basic system of equations includes the Liouville equation for the density  $\rho$

$$\partial\rho/\partial t + \dot{\mathbf{q}}^T(\partial\rho/\partial\mathbf{q}) + \dot{\mathbf{p}}^T(\partial\rho/\partial\mathbf{p}) = 0 \quad (1)$$

and the kinematic equations for the velocities  $\dot{\mathbf{q}}$  and momentum rates  $\dot{\mathbf{p}}$  obtained from the energy considerations:

$$\begin{aligned} \dot{\mathbf{q}} &= \dot{\mathbf{q}}(\mathbf{q}, \mathbf{p}) \\ \dot{\mathbf{p}} &= \dot{\mathbf{p}}(\mathbf{q}, \mathbf{p}) \end{aligned} \quad (2)$$

The interatomic potentials defined for every pair of atoms ( $i, j$ ) separated by

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the vector  $\mathbf{R}_{ij}$  yield the interaction forces  $\mathbf{f}_{ij}$  and corresponding stress dyadics  $\sigma_{ij}$

$$\mathbf{f}_{ij} = \text{grad } U_{ij}(1 + \dots) \tag{3}$$

$$\sigma_{ij} = \mathbf{f}_{ij}\mathbf{R}_{ij}^T \approx \text{grad } U_{ij}\mathbf{R}_{ij}^T \tag{4}$$

The macroscopic stress tensor consists of two parts

$$\sigma = \sigma_{(K)} + \sigma_{(U)} \tag{5}$$

The kinetic part (important for gases but negligible for condensed systems) reads

$$\sigma_{(K)} = (c/m) [\langle \mathbf{p}\mathbf{p}^T \rangle - \langle \mathbf{p} \rangle \langle \mathbf{p} \rangle^T] \tag{6}$$

and the interaction part

$$\sigma_{(U)} = c \langle \mathbf{f}\mathbf{R}^T \rangle \approx \langle \text{grad } \mathbf{U}\mathbf{R}^T \rangle \tag{7}$$

In the above  $c$  denotes the concentration of kinetic units in the system,  $m$  is their mass and  $\langle \rangle$  denote averaging over the entire ensemble of particles.

Application of this approach to more complex systems meets with serious difficulties. Dahler and Scriven<sup>8</sup> discussed the case of fluids with polyatomic molecules as kinetic units and assumed single interaction potentials. It is not certain, however, if such potentials (assumed in general to be non-central but not defined explicitly) have clear physical significance.

Many more difficulties arise when macromolecular systems are considered. Large chain molecules having many internal degrees of freedom can hardly be modelled as simple kinetic units with single interaction potentials. If, on the other hand, we choose as kinetic units the individual atoms forming macromolecules (and solvent molecules, if present in the system) we are faced with a number of non-equivalent interacting atom pairs: two atoms belonging to the same macromolecule, two atoms from different macromolecules etc. All this excludes the possibility of building up a molecular theory of polymer systems on the basis of 'pure' unchanged statistical mechanics without introducing any additional, simplified concepts.

The theories involving a number of additional model assumptions and simplifications will necessarily be less fundamental than those based on 'pure'

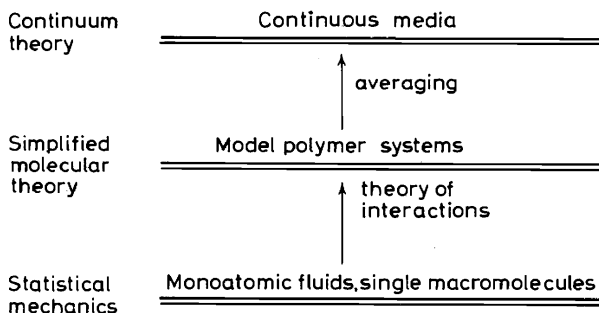


Figure 1.

statistical mechanics, and will occupy an intermediate position between statistical mechanics and the theory of continuum (Figure 1). If such an intermediate theory is still to be considered a really molecular theory, the simplified structural model should be physically realistic, i.e. consistent with the actual structure of corresponding real systems and each simplified interaction concept should possess a clear physical significance, if possible derived from statistical mechanical considerations. Unfortunately many published theories of polymer systems do not conform to these requirements; they include arbitrary and unverifiable assumptions about the structure of the system and interactions within it.

In the simplified molecular theories some structural units specific for the considered system are chosen to replace atoms in the statistical mechanical treatment. The role of such units can be played by individual macromolecules, chain segments, molecular clusters etc. The configuration of every unit is described with the aid of  $N$  variables,  $\mathbf{u} = (u_1, u_2, \dots, u_N)$  replacing variables  $\mathbf{q}$  and  $\mathbf{p}$  in pure statistical mechanics. A time-dependent distribution function for the single structural unit is determined by the equation of continuity in  $N$ -dimensional configurational space

$$\partial\Psi/\partial t + (\partial^T/\partial\mathbf{u})(\Psi\dot{\mathbf{u}}) = \dot{\Psi}_{\text{kin}} \quad (8)$$

It may be noted that in equation 8 there appears, beside the usual transient and divergence terms, a kinetic term, equal to the net rate of production of structural units within the system. The basic equations of the theory include also the kinematic equations

$$\dot{\mathbf{u}} = \dot{\mathbf{u}}(\mathbf{u}, \Psi, t) \quad (9)$$

and the equation describing the kinetics of formation and dissociation of structural units

$$\dot{\Psi}_{\text{kin}} = \dot{\Psi}_{\text{kin}}(\mathbf{u}, \dot{\mathbf{u}}, \Psi) \quad (10)$$

both to be formulated on the basis of independent considerations.

Consideration of the interactions between some 'interaction centres' in the structural units, yields the interaction tension

$$\mathbf{f} = \mathbf{f}(\mathbf{u}, \dot{\mathbf{u}}, \Psi) \quad (11)$$

which, multiplied by the corresponding vector  $\mathbf{R}$ , yields the local stress dyadics

$$\sigma_{\text{loc}} = c\mathbf{f}\mathbf{R}^T \quad (12)$$

The macroscopic stress tensor (like any other macroscopic, configuration-dependent characteristics of the system)  $\sigma$  is obtained through averaging of the local characteristics over the distribution function  $\Psi$

$$\sigma = \langle \sigma_{\text{loc}} \rangle = \int \dots \int \sigma_{\text{loc}} \Psi(\mathbf{u}, t) d\mathbf{u} \quad (13)$$

The equation of continuity, the kinematic, kinetic and dynamic equations (equation 11) make the fundamental system of the theory and should be solved simultaneously with proper initial and boundary conditions. The above scheme enables one to allow for very different external conditions including non-homogeneous and non-steady-state deformations, time-dependent parameters etc.<sup>5</sup>. In later sections of this paper we will formulate

the fundamental equations of the theory of dilute polymer solutions and entanglement networks.

### SOME SIMPLIFIED CONCEPTS IN MACROMOLECULAR INTERACTIONS

For the construction of molecular theories of polymer systems the complex molecular interactions must be simplified to obtain the more tractable relations required for the dynamic (equation 11) and kinematic equations. It would go beyond the scope of the present paper to give a full review of all possible interaction concepts in this field; we will discuss only some examples which will be used later in deriving the theories of solutions and networks.

#### Intramolecular interactions within chain macromolecules

Statistical considerations can yield quite exact conformation distributions for linear macromolecules with given bond angles,  $\alpha$ , bond lengths,  $z$ , and rotation-dependent potentials  $U(\varphi)$ . The appropriate calculation methods and results may be found in the literature<sup>9-11</sup>. The conformation problems for electrically charged macromolecules (polyelectrolytes) have also been treated statistically (cf. ref. 12 and the references cited therein).

When the theory of *polymer systems*, rather than of isolated macromolecules, is to be constructed, the more exact (and more complicated) conformation distributions must be replaced by simplified models. One of the more popular models of this kind is the so-called 'freely jointed chain' whose end-to-end vector distribution  $\Psi(\mathbf{h})$  can be described with the aid of the two-parameter formula<sup>13</sup>

$$\Psi_0(\mathbf{h}) = C \exp \left[ -(l/a) \int_0^{h/l} L^*(x) dx \right] \quad (14)$$

where  $L^*(x) = 3x + \frac{2}{5}x^3 + \dots$  is the inverse Langevin function,  $C$  is a normalization constant,  $l$  is the contour length of the macromolecule (i.e. the length of the fully extended chain),  $a$  is the length of the statistical (Kuhn) chain segment. The latter characteristic can be related directly to the molecular data  $z$ ,  $\alpha$  and  $U(\varphi)$ . For symmetrical and not very high potential barriers and for sufficiently long chains the Taylor formula holds<sup>14</sup>

$$a[z, \alpha, U(\varphi)] = z(1 + \cos \alpha)(1 - \cos \alpha)^{-1}(1 + \langle \cos \varphi \rangle)(1 - \langle \cos \varphi \rangle)^{-1} \quad (15)$$

where the average cosine of the rotation angle  $\varphi$  is related to the potential function  $U(\varphi)$

$$\langle \cos \varphi \rangle = \int_0^{2\pi} \cos \varphi \exp [-U(\varphi)/kT] d\varphi / \int_0^{2\pi} \exp [-U(\varphi)/kT] d\varphi \quad (16)$$

From the definition of the contour length it follows that

$$l = nz \cos \alpha \quad (15a)$$

where  $n$  is the number of bonds in the chain.

The simple two-parameter distribution (equation 14) allows for the bond lengths, valence angles and rotation hindrances of the macromolecular chain. The natural consequence of this distribution is the elastic force which appears in equilibrium in the deformed chain

$$\mathbf{f}_{el} = -kT \text{grad} \ln \Psi_0 = (kT\mathbf{h}/ah) L^*(h/l) = (3kT\mathbf{h}/la) \left[ 1 + \frac{3}{5}(h^2/l^2) + \dots \right] \quad (17)$$

The above model does not predict, however, the elastic force arising due to the energy differences between various rotational isomers.

The existence of some rotational energetic barriers to be overcome in the process of chain deformation (i.e.  $dU/d\varphi \neq 0$ ) also leads to some non-equilibrium force  $\mathbf{f}_v$  when the chain is subjected to some deformation rate ( $dh/dt \neq 0$ )

$$\mathbf{f}_v = \text{const.} [(dh/dt) + a_1(dh/dt)^2 + \dots] (\mathbf{h}/h) \quad (18)$$

This effect was first proposed by W. Kuhn and H. Kuhn<sup>15</sup> who called it 'internal viscosity'. Taking into account that the constant in equation 18 is inversely proportional to the number of chain segments capable of rotation (i.e. inversely proportional to the contour length,  $l$ ), confining ourselves to the consideration of small deformation rates only (linear term in equation 18), and writing the deformation rate in vector form, we obtain from equation 18

$$\mathbf{f}_v \approx \gamma l^{-1} (\mathbf{h}^T \dot{\mathbf{h}} / h^2) \mathbf{h} \quad (18a)$$

The constant  $\gamma$  in equation 18a is determined only by the chemical structure of the macromolecule but is practically independent of its molecular weight. In principle  $\gamma$  can be found (or, compared for several polymers) experimentally, using flow birefringence techniques<sup>16</sup>.

There is no exact theory which could relate the phenomenological concept of internal viscosity to primary molecular characteristics. In the approximation of the absolute reaction rate theory<sup>17</sup> one could expect the coefficient  $\gamma$  to be related to the difference of maximum and minimum values of the potential function,  $\Delta U = U_{\text{max.}} - U_{\text{min.}}$ , acting as an 'activation energy' for the deformation process

$$\gamma \approx \text{const.} \exp(-\Delta U/kT) \quad (19)$$

### Intermolecular interactions in polymer systems

In systems containing both polymer and low-molecular substances, the solvent, having molecules several orders of magnitude smaller than the macromolecules of polymer, can be treated as a viscous continuum. In this approximation the discrete polymer-solvent interactions can be described by the continualized concept of *polymer-solvent friction*. Such a frictional force per macromolecule with contour length  $l$  may be written in the form

$$\mathbf{f}_{p-s} = \zeta l \Delta \mathbf{v} [1 + \alpha_1 |\Delta \mathbf{v}| + \alpha_2 (\Delta \mathbf{v})^2 + \dots] \quad (20)$$

where  $\Delta \mathbf{v}$  is the actual velocity difference between the macromolecule and solvent, and  $\zeta$  is the molecular friction coefficient per unit contour length of the macromolecule surrounded by solvent.  $\zeta$  depends on the molecular structures of polymer and solvent, as well as on the temperature of the system. The concept of polymer-solvent friction was introduced to polymer physics by W. Kuhn and H. Kuhn<sup>18</sup> and has since been widely used in the theory of dilute polymer solutions. In principle, the coefficients  $\zeta$  can be determined experimentally for any combination of polymer and solvent from viscosity or diffusion measurements.

According to the assumption of continuity, the *interactions between*

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*solvent molecules* are usually considered to produce linear stress effects, as in any Newtonian, viscous fluid.

The interactions of distant parts of the same macromolecule, or those of two different macromolecules in a rather dilute solution are often treated as disturbances of the velocity field in the viscous continuum (solvent). According to the well known Oseen theory the velocity disturbance  $\Delta v_p$  at some point  $p$  is determined by friction forces in all points (friction centres)  $q$  within the system<sup>19</sup>. Such a type of intermolecular interactions (so-called 'hydrodynamic interactions') was widely discussed in the theories of dilute polymer solutions; in concentrated systems, however, it seems to be negligible in comparison with *polymer-polymer contact friction*. For two polymer molecules (or various parts of the macromolecule) coming into close contact one with another, one can write, in an analogy to equation 20

$$f_{p-p} = \xi \Delta v [1 + \beta_1 |\Delta v| + \beta_2 (\Delta v)^2 + \dots] \quad (21)$$

where  $\xi$  is the molecular friction coefficient per one polymer-polymer contact. Such a mechanism could be responsible for the behaviour of very concentrated systems of rigid asymmetrical particles, but apparently contributes to the behaviour of all concentrated polymer systems.

Quite a different kind of polymer-polymer interaction is provided by a *localized (energetic) junction*, i.e. a chemical or quasicomical bond [Figure 2(a)]. If we neglect the small oscillations within the range of such a bond, the energetic junction may be considered to be strictly localized in a definite position with respect to both the participating macromolecules and their relative velocity,  $\Delta v$  (sliding velocity) is equal to zero [Figure 2(b)]. The junction is assumed to have a *finite dissociation energy*: when the critical energy level is attained (due to the supply of thermal, mechanical, etc. energy from outside) the junction breaks instantaneously and  $\Delta v \rightarrow \infty$ .

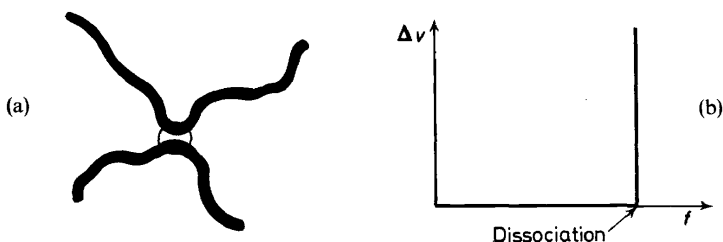
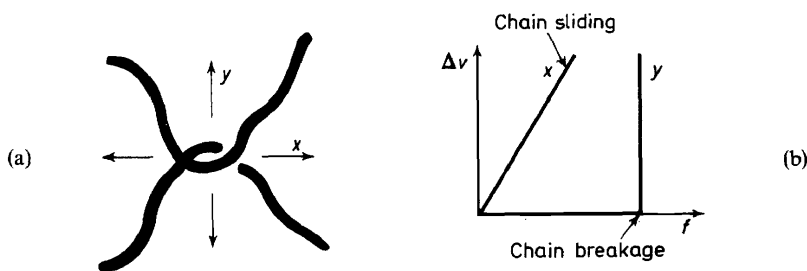


Figure 2. Localized (energetic) junction: (a) schematic, (b) delocalization rate versus applied energy (or tension).

A different behaviour can be expected for the system of interpenetrating loops forming *entanglement junctions* (Figure 3). This kind of interaction, specific for long, flexible chains, leads to junctions which are not localized but capable of sliding (with some contact friction) along the chains involved. The dynamic behaviour of entanglement junctions is anisotropic: in the direction corresponding to the tightening of the loop ( $y$ ) the junction is practically localized and behaves like an energetic junction with dis-

sociation energy determined by the breaking of the chains. Along the chains (direction  $x$ ) chain sliding with contact friction (cf. equation 21) can be observed. This situation is drawn schematically in *Figure 3(b)*.



*Figure 3.* Non-localized (entanglement) junction: (a) schematic, (b) delocalization rate versus applied tension.

### EXAMPLES OF APPLICATION TO VARIOUS POLYMER SYSTEMS

The general lines of procedure outlined above form a framework on which theories of various polymer systems can be constructed. Of course, it is not the only approach possible in this field, but it seems to provide a rational and convenient basis for simplified molecular considerations.

The number of structural systems studied along these or similar lines is rather small, however. One can name here dilute suspensions of rigid particles<sup>20-28</sup> and dilute polymer solutions with various kinds of intramolecular interactions but neglected interactions between individual macromolecules<sup>29-40</sup>. The other extreme case is a permanent, macromolecular network analysed by many authors since the early thirties (cf. ref. 41 and the literature cited therein). 'Hauber' networks (i.e. systems formed of closed, interpenetrating loops) were recently discussed by Frisch and Prager<sup>42</sup> and by Edwards<sup>43</sup>. Both the above models provide a basis for the molecular interpretation of rubber elasticity.

The theory of 'temporary' networks with localized junctions as developed by Green and Tobolsky<sup>44</sup>, Scott and Stein<sup>45</sup>, Yamamoto<sup>46</sup> and Lodge<sup>47</sup> seems to be appropriate for systems with strongly polar interactions (polar gels, vulcanized rubbers with chain scission etc.).

There is no adequate theory for concentrated polymer solutions and melts where entanglement interactions and chain sliding seem to play the determining role. The papers published by Bueche<sup>1</sup>, Graessley<sup>2</sup>, Hayashi<sup>3</sup>, and Hoffmann<sup>48</sup> cannot be discussed here as examples involving arbitrary assumptions<sup>1,2</sup> or formal errors<sup>3,48</sup>. Extension of the Rouse theory of dilute solutions<sup>33</sup> to cover concentrated systems with entanglement interactions<sup>49-51</sup> is physically incorrect and will be discussed below in detail. Recently, more systematic studies on the theory of entanglement networks were started in the author's laboratory. Some results have been published<sup>52-54</sup>



and will be discussed in the next section; completion of the theory still requires much work to be done.

### The theory of dilute solutions and entanglement networks

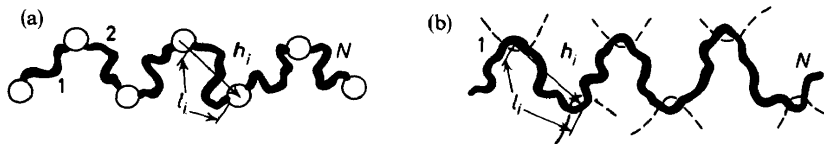
Proceeding along the lines set out above we will discuss now the molecular theory of two polymer systems: dilute solutions containing flexible macromolecules in a viscous solvent, and entanglement networks formed of similar macromolecules in a highly concentrated system. The comparison of these two systems seems to be especially interesting. The theory of dilute solutions is well developed and widely appreciated thus making a good example for the illustration of more general considerations. In spite of some formal similarities between the molecular models involved in these two theories (see *Figure 4* below), the macromolecules in network systems behave quite differently to those in dilute solutions. Nevertheless several papers have been published in which the Rouse theory of dilute solutions corrected for 'limited mobility' or 'effective friction coefficients' was applied to the description of network systems<sup>49-51</sup>.

The first difference between the two molecular systems involved lies in the way in which external forces applied to the boundary of the sample are transmitted to the individual macromolecules. In systems with separated macromolecules (dilute solutions) forces are transmitted *through the viscous continuum (solvent)* as friction forces. In a coherent network system formed of macromolecules connected at some junctions, the force is transmitted *through the junctions* and friction forces, if present, contribute to the dynamic reaction of the individual macromolecules or their parts.

In contrast to dilute solutions where all 'subchains' [see *Figure 4(a)*] had *ex definitione* the same molecular weight (and contour lengths,  $l$ ), network chains, i.e. portions of the primary macromolecule contained between adjacent entanglement junctions, have different and time-dependent lengths,  $l$ . Therefore the molecular theory of such systems should consider the distribution of contour lengths,  $l$ , as independent variables, and allow for sliding rates,  $\dot{l}$ , as kinematic characteristics in addition to the usually considered junction-to-junction vectors,  $\mathbf{h}$ , and junction velocities,  $\dot{\mathbf{h}}$ .

Last, but not least, the temporary network systems involve some kinetic processes of junction breakage and re-formation, absent from dilute solutions with separated macromolecules.

Let us proceed with the systematic discussion of both theories. We will consider the configuration distributions for a primary macromolecule consisting of  $N$  subchains [dilute solutions, *Figure 4(a)*], or,  $N$  network chains [entanglement network, *Figure 4(b)*].



*Figure 4.* Molecular models of chain macromolecules: (a) in dilute solutions,  $N$  subchains with friction centres; (b) in concentrated solutions or melts;  $N$  network chains with entanglement junctions.

Thus, the set of independent configuration variables for dilute solution theory includes  $3N$  components of subchain vectors  $\mathbf{h}_i$  while the contour lengths of all chains are equal to  $l_i = L/N$  ( $L$  is the contour length of the entire macromolecule). In the network system there are  $4N - 1$  independent variables:  $3N$  components of vectors  $\mathbf{h}_i$  and  $N$  contour lengths,  $l_i$  together with the normalization condition

$$\sum_{i=1}^N l_i = L \quad (22)$$

The distribution function for dilute solutions is defined as the probability density in  $3N$ -dimensional configurational space

$$\Psi(\mathbf{h}, t) d\mathbf{h} = dn/n_0 \quad (23)$$

whereas that for entanglement networks

$$\Psi^*(\mathbf{h}, \mathbf{l}, t) d\mathbf{h}d\mathbf{l} = dn/n_0 \quad (24)$$

where the asterisk denotes the characteristics related to network systems and  $\mathbf{h}, \mathbf{l}$  are vectors

$$\begin{aligned} \mathbf{h} &= (x_1, y_1, z_1, x_2, \dots, z_N) \\ \mathbf{l} &= (l_1, l_2, \dots, l_N) \end{aligned}$$

The tension in the  $i$ th subchain of the macromolecule in a dilute solution,  $\mathbf{f}_i$  consists of the elastic, statistical and internal viscosity terms

$$\mathbf{f}_i = kT[(3\mathbf{h}_i/la)(1 + \frac{3}{2}h_i^2/l^2 + \dots) + (\partial/\partial\mathbf{h}_i)\ln\Psi] + (\gamma/l)(\mathbf{h}_i^T\dot{\mathbf{h}}_i/h_i^2)\mathbf{h}_i \quad (25)$$

For simplicity, the hydrodynamic interactions, usually considered in the theory of dilute solutions, have been omitted.

Similar tension in the  $i$ th network chain of an entangled system includes, beside the above terms, also the contributions of chain sliding,  $\dot{\mathbf{l}}$

$$\mathbf{f}_i^* = \mathbf{f}_i - \frac{1}{2}K(\zeta, \xi)\mathbf{h}_i\mathbf{B}_{ij}\dot{l}_j + \zeta\mathbf{C}_{ij}\dot{l}_j \quad (26)$$

where  $K$  is the total (polymer-solvent and polymer-polymer) contact friction coefficient and the matrices are associated with contact friction along the network chain ( $\mathbf{B}$ ) and friction in the entanglement junctions alone ( $\mathbf{C}$ )<sup>5,3</sup>.

The kinematic equations for dilute solutions are obtained directly from the force balance condition for the  $i$ th friction centre (bead) joining the  $i$ th and  $(i + 1)$ th subchains. In our notation the force balance condition assumes the form

$$\mathbf{f}_{\text{ext}}^i = -\mathbf{f}_{\text{fr}}^i = \mathbf{f}_{i+1} - \mathbf{f}_i \quad (27)$$

or

$$\mathbf{f}_{i+1} \doteq \mathbf{f}_i + \mathbf{f}_{\text{fr}}^i = 0 \quad (27a)$$

where  $\mathbf{f}_{\text{ext}}^i$  is the external force and  $\mathbf{f}_{\text{fr}}^i$  is the friction force acting on the  $i$ th bead (cf. equation 20).  $\mathbf{f}_i, \mathbf{f}_{i+1}$  are the tensions of the chains  $i$  and  $i + 1$  respectively as defined in equation 25. Using a linear (Stokesian) approximation for the friction force and expressing the effective velocity difference at the  $i$ th bead through junction velocities  $\dot{\mathbf{h}}_i$ , one obtains the well known result

$$\mathbf{h}_i = \dot{\mathbf{e}}_0 \mathbf{h}_i - (\zeta l)^{-1} A_{ij} \mathbf{f}_j \tag{28}$$

and, from the definition of the subchain model,

$$\dot{l}_i \equiv 0 \tag{29}$$

$\dot{\mathbf{e}}_0$  is the macroscopic relative velocity gradient and  $A$  is the matrix

$$A = \begin{pmatrix} 1 & -1 & & & 0 \\ -1 & 2 & -1 & & \\ 0 & -1 & 2 & -1 & \\ 0 & \dots & \dots & \dots & \dots \end{pmatrix} \tag{30}$$

For the network system, where external forces are transmitted through network chains rather than through the solvent, the force balance condition for some  $i$ th junction reads<sup>53</sup>

$$\mathbf{f}_{\text{ext}} = \mathbf{f}_i^* - \mathbf{f}_i^* = \mathbf{f}_j^* - \mathbf{f}_{j+1}^* \tag{31}$$

where  $\mathbf{f}_i^*, \mathbf{f}_{i+1}^*$  are full tensions (cf. equation 26) of the network chains  $i, i + 1$  belonging to the macromolecule considered, and  $\mathbf{f}_j^*, \mathbf{f}_{j+1}^*$  are similar tensions of the other chains belonging to a different macromolecule participating in the junction. Note that unlike  $\mathbf{f}_p$ , the tensions in network chains,  $\mathbf{f}_i^*$  include some frictional terms. In an analogy to equation 27a, instead of equation 31 we may write

$$\mathbf{f}_{i+1} - \mathbf{f}_i - \mathbf{f}_{\text{fr}}^{*i} = \mathbf{f}_{\text{ext}} \tag{31a}$$

where  $\mathbf{f}_{\text{fr}}^{*i}$  is the total friction force in the junction ‘ $i$ ’.

It is evident that, while in dilute solutions the frictional force  $\mathbf{f}_{\text{fr}}$  acted as the external force transmitted through the solvent from the boundary, in the network system  $\mathbf{f}_{\text{fr}}^*$  is simply a part of the response of the chain to the external force applied through the other network chains connected by the junction. Both these situations are illustrated schematically in Figure 5.

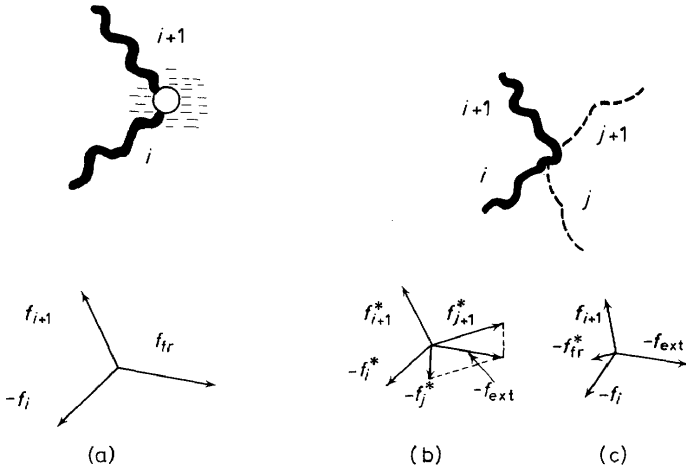


Figure 5. Force balance for the  $i$ th interaction centre: (a) in dilute solutions; (b), (c) in entangled systems.  $\mathbf{f}_{\text{ext}}$  is an external force,  $\mathbf{f}_{\text{fr}}$  is a frictional force,  $\mathbf{f}_p, \mathbf{f}_{i+1}, (\mathbf{f}_i^*, \mathbf{f}_{i+1}^*)$  are tensions of the subchains (network chains).

The difference between the force balance equations leads to quite different kinematics of macromolecules in dilute solutions and networks respectively. Junction velocities  $\dot{\mathbf{h}}_i$  for the network system cannot be obtained from the force balance (equation 31 or 31a) because  $\mathbf{f}_{\text{ext}}^i$  is not defined explicitly and the equation involves two unknowns:  $\dot{\mathbf{h}}$  and  $\dot{l}$ . We will note, however, that due to the coherence of the network system the local velocity gradients  $\dot{\mathbf{e}}_i$  must be on average equal to the macroscopic velocity gradient  $\dot{\mathbf{e}}_0$ . We will assume in a first approximation that all  $\dot{\mathbf{e}}_i$  are identical

$$\dot{\mathbf{e}}_i \approx \dot{\mathbf{e}}_0 \tag{32}$$

and therefore

$$\dot{\mathbf{h}}_i = \dot{\mathbf{e}}_0 \mathbf{h}_i \tag{33}$$

The other kinematic variable,  $\dot{l}$  can be obtained from the simplified force balance equation, putting  $\dot{\mathbf{h}}$  from equation 33 and averaging the interactions with other macromolecules<sup>54</sup>. The sliding rates result in the following form

$$\dot{l}_i = \mathbf{D}_{ij} |\mathbf{f}_j| \tag{34}$$

where  $\mathbf{D} = \mathbf{D}(K, \xi, \mathbf{B}, \mathbf{C})$  is a matrix depending on the contact and entanglement frictions and  $\mathbf{f}_j$  are chain tensions including no friction terms (cf. equations 25 and 26).

In the extreme case when the entanglement friction can be neglected as compared with contact friction ( $\xi \ll Kh$ ) one obtains

$$\mathbf{D} = K^{-1} \mathbf{E} h^{-1} \tag{35a}$$

and in the other case (contact friction negligible,  $\xi \gg Kh$ )

$$\mathbf{D} = \xi^{-1} \mathbf{A} \tag{35b}$$

with

$$\mathbf{E} = \begin{pmatrix} 2 & & & \mathbf{0} \\ -4 & 2 & & \\ 4 & -4 & 2 & \\ 12 & 4 & -4 & 2 \\ \dots & \dots & \dots & \dots \end{pmatrix} \tag{36}$$

The kinematic equations for network systems (equations 33 and 34) are quite different to those for dilute solutions (equations 28 and 29), even although in the 'purely contact' case (equation 35a) there appears the same transformation matrix  $\mathbf{A}$  known from the theory of dilute solutions. Accordingly, the physical behaviour of both systems may be expected to differ.

The other element of the theory is the kinetics of formation and dissociation of structural elements. There is no such process in dilute solutions and one can write:

$$\Psi_{\text{kin}} \equiv 0 \tag{37}$$

On the other hand, in entanglement networks, the existence of free chain ends makes possible sliding-out and sliding-in processes forming the basis for a non-zero kinetic term (Figure 6). The kinetic terms include the net change of the distribution function,  $\Psi_{\text{kin}}^*$ , and the rate of variation of the number of

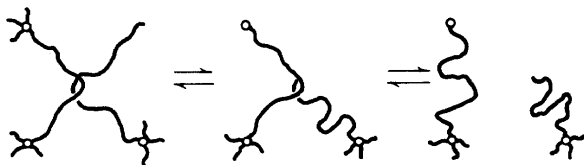


Figure 6. Sliding-in, sliding-out, mechanism of kinetic processes in entanglement networks with free chain ends.

junctions per primary macromolecule,  $\dot{N}$ . The theory of these processes is not yet complete but the general form of  $\Psi_{\text{kin}}^*$  may be expected to involve several integral expressions

$$\Psi_{\text{kin}}^*(\mathbf{h}, \mathbf{l}, \dot{\mathbf{h}}, \dot{\mathbf{l}}, \Psi) = \sum_k \int \dots \int {}^k F(\mathbf{h}, \bar{\mathbf{h}}, \mathbf{l}, \bar{\mathbf{l}}, \dots, \mathbf{l}, \dot{\mathbf{l}}) \Psi^*(\mathbf{h} + \bar{\mathbf{h}}, \mathbf{l} + \bar{\mathbf{l}}) \Psi^*(\bar{\mathbf{h}}, \bar{\mathbf{l}}) d\bar{\mathbf{h}} d\bar{\mathbf{l}} \quad (38)$$

where  ${}^k F(\mathbf{h}, \dots)$  is the frequency factor for the  $k$ th molecular process responsible for dissociation or re-formation of a network junction. The breakage or formation of a junction is a cooperative process involving several network chains belonging to two different macromolecules. Hence the convolution forms in equation 38. It is worth noting that similar kinetic expressions for energetic networks were obtained by Scott and Stein<sup>45</sup>.

Now, the equations of continuity for both molecular models can be written in the form

$$\partial \Psi / \partial t + (\partial^T / \partial \mathbf{h}) (\Psi \dot{\mathbf{h}}) = 0 \quad (39)$$

for dilute solutions, and

$$\partial \Psi^* / \partial t + (\partial^T / \partial \mathbf{h}) (\Psi^* \dot{\mathbf{h}}) + (\partial^T / \partial \mathbf{l}) (\Psi^* \dot{\mathbf{l}}) = \dot{\Psi}_{\text{kin}}^* - (\partial \Psi^* / \partial N) \dot{N} \quad (40)$$

for network systems. With kinematic characteristics from equations 28, 33 and 34, equations of continuity assume the form

$$\partial \Psi / \partial t + (\partial^T / \partial \mathbf{h}) [\Psi \dot{\mathbf{e}}_0 \mathbf{h} + (k_T / \zeta l) \mathbf{A} \{ (3 \Psi \mathbf{h} / a l) + (\partial \Psi / \partial \mathbf{h}) \}] = 0 \quad (39a)$$

and

$$\begin{aligned} \frac{\partial \Psi^*}{\partial t} + \frac{\partial^T}{\partial \mathbf{h}} [\Psi^* \dot{\mathbf{e}}_0 \mathbf{h}] + kT \frac{\partial^T}{\partial \mathbf{l}} \mathbf{D} \left[ \frac{3 \Psi^* |\mathbf{h}|}{a l} + |\partial \Psi^* / \partial \mathbf{h}| \right] \\ = \dot{\Psi}_{\text{kin}}^*(\mathbf{h}, \mathbf{l}) - \frac{\partial \Psi^*}{\partial N} \dot{N} \end{aligned} \quad (40a)$$

for dilute solutions and networks respectively.

To find the local and macroscopic stress tensors we will consider the individual beads (subchain model) or network junctions (entanglement

network) as the 'interaction centres'. The tensions  $f_i$  and  $f_i^*$  as given by equations 25 and 26 can thus be identified with pair-interaction forces for the centres 'i' and 'i - 1'. The interactions of distant elements are included in  $f_i^*$  as frictional contact terms. At the same time, the junction-to-junction, or subchain, vectors  $h_i$  can be identified with vectors  $\mathbf{R}$  from equation 12. Thus the local stress dyadics for the models considered assume the form

$$\sigma_{loc} = c f_i h_i^T \quad (41)$$

for dilute solutions, and

$$\sigma_{loc}^* = v(t) f_i^* h_i^T \quad (42)$$

for network systems.  $c$  denotes the concentration of subchains, and  $v(t)$  is the time-dependent concentration of network chains in the system considered. Averaging over the corresponding distribution functions yields the macroscopic stress tensor for dilute solutions

$$c^{-1}[\sigma + ckTI] = (3kT/al) \langle \mathbf{h}h^T(1 + \dots) \rangle + (\gamma/l) \langle \mathbf{h}^T \mathbf{h}(\mathbf{h}h^T)/h^2 \rangle \quad (43)$$

In the case of networks with non-localized junctions two additional terms appear associated with chain sliding  $l$

$$v^{-1}[\sigma^* + vkTI] = (3kT/a) \langle \mathbf{h}h^T(1 + \dots)/l \rangle + \gamma \langle \mathbf{h}^T \mathbf{h}(\mathbf{h}h^T)/lh^2 \rangle - \frac{1}{2} K \langle \mathbf{B}l\mathbf{h}h^T \rangle + \xi \langle \mathbf{C}l\mathbf{h}h^T \rangle \quad (44)$$

The other difference between the stress tensors  $\sigma$  and  $\sigma^*$  concerns the averaging which in the case of dilute solutions involves only variables  $\mathbf{h}$  whereas for networks both  $\mathbf{h}$ s and  $l$ s are considered.

### SOME COMMENTS ON THE THEORY OF DILUTE SOLUTIONS AND NETWORKS

Since the ultimate solutions of the continuity equation for entanglement networks is not yet available, the averages in equation 44 cannot be given in an explicit form and the detailed discussion of the stress tensor is not possible at the present moment. However, the comparison of the network theory with the theory of dilute solutions enables one to draw several general conclusions.

(1) Network theory with non-localized, entanglement junctions predicts non-linear viscoelastic behaviour, stress relaxation and steady-state flow effects dependent on the molecular weight of primary macromolecules and polymer concentration.

(2) The continuity equation for dilute solutions (equations 39 and 39a) is linear and separable into time and space parts. Therefore the time dependence of the distribution function  $\Psi$  (and all the configuration-dependent physical characteristics) can be discussed in terms of the linear theory of viscoelasticity. This is not true for network systems where non-linear terms appear in the kinetic contribution; in general, the linear viscoelasticity theory is not applicable to such systems unless some additional simplifications are introduced.

(3) In the range of Gaussian chain statistics and with neglected internal

viscosity, the stress tensor in dilute solutions,  $\sigma$  is uniquely related to the optical and electric polarizability tensors, all linear functions of the average dyadics  $\mathbf{h}\mathbf{h}^T$ . In network systems in the same approximation other stress contributions appear due to chain sliding and the relation of stress to polarizability is not insignificant.

(4) Within the Gaussian range and with neglected internal viscosity the continuity equation for dilute solutions can easily be normalized through linear transformation of the independent variable  $\mathbf{h}$ . Assume the orthogonal transformation

$$\mathbf{h} \rightarrow \mathbf{Q}\boldsymbol{\eta} \quad (45)$$

such that

$$\begin{aligned} \mathbf{Q}^T\mathbf{Q} &= \mathbf{I} \\ \mathbf{Q}^T\mathbf{A}\mathbf{Q} &= \mathbf{M}_{(\text{diag})} \end{aligned} \quad (46)$$

Application of this transformation to the variable  $\mathbf{h}$  in equation 39a yields the equation of continuity in normal coordinates (the matrix  $\mathbf{M}$  is diagonal)

$$\frac{\partial \Psi}{\partial t} + \frac{\partial^T}{\partial \boldsymbol{\eta}} \left[ \Psi \dot{\mathbf{e}}_0 \boldsymbol{\eta} + \frac{kT}{\zeta l} \mathbf{M} \left( \frac{3\Psi}{al} \boldsymbol{\eta} + \frac{\partial \Psi}{\partial \boldsymbol{\eta}} \right) \right] = 0 \quad (39b)$$

Let us examine the possibility of a similar transformation in the case of network theory. We will assume for the time being that the kinetic terms on the RHS of equation 40a are linear, and that the matrix  $\mathbf{D}$  in the kinetic equations can be diagonalized by some orthogonal transformation  $\mathbf{P}$

$$\begin{aligned} \mathbf{P}^T\mathbf{P} &= \mathbf{I} \\ \mathbf{P}^T\mathbf{D}\mathbf{P} &= \mathbf{S}_{(\text{diag})} \end{aligned} \quad (47)$$

Now, both the configuration variables,  $\mathbf{h}$  and  $\mathbf{l}$  must be transformed with  $\mathbf{P}$

$$\begin{aligned} \mathbf{h} &\rightarrow \mathbf{P}\boldsymbol{\eta} \\ \mathbf{l} &\rightarrow \mathbf{P}\boldsymbol{\lambda} \end{aligned} \quad (48)$$

With these transformations equation 40a yields

$$\begin{aligned} \frac{\partial \Psi^*}{\partial t} + \frac{\partial^T}{\partial \boldsymbol{\eta}} (\Psi^* \dot{\mathbf{e}}_0 \boldsymbol{\eta}) + kT \frac{\partial^T}{\partial \boldsymbol{\lambda}} \mathbf{P}^T \mathbf{D} \left[ \frac{3\Psi^* \mathbf{P} |\boldsymbol{\eta}|}{a\mathbf{P}\boldsymbol{\lambda}} + \mathbf{P} \left| \frac{\partial \Psi^*}{\partial \boldsymbol{\eta}} \right| \right] \\ = \Psi_{\text{kin}}^* (\mathbf{P}\boldsymbol{\eta}, \mathbf{P}\boldsymbol{\lambda}) - \left( \frac{\partial \Psi^*}{\partial N} \right) \dot{N} (\mathbf{P}\boldsymbol{\eta}, \mathbf{P}\boldsymbol{\lambda}) \end{aligned} \quad (40b)$$

Even putting aside the kinetic terms (which in general are non-linear) and assuming  $\mathbf{D}$  to be diagonalizable (which is not always true;  $\mathbf{D}$  may be unsymmetrical, see equation 36), the transformation of the continuity equation using the method of normal coordinates is not possible because of the non-linear terms

$$\mathbf{P}^T \mathbf{D} (\mathbf{P} |\boldsymbol{\eta}| / \mathbf{P}\boldsymbol{\lambda})$$

appearing as the result of simultaneous transformation of junction vectors  $\mathbf{h}$  and contour lengths  $l$ . The normal coordinates method, so fruitful in the (essentially linear) theory of dilute solutions, appears to be inapplicable for network systems.

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