Molecular Theories of Dense *vs.* Dilute Polymer Systems

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ABSTRACT: It has been shown that kinematics and dynamics of macromolecules involved in network systems (commonly recognized as appropriate models of condensed systems) are entirely different from those for isolated macromolecules in dilute solutions. Consequently, molecular theories of condensed systems cannot be obtained by simple extension of the dilute solution theory. In network systems the mobility matrices (which control viscoelastic behavior of dilute solutions) are indeterminate and network theories based on the modification of mobility matrices are incorrect in principle. Extensions of the Zimm-Rouse theory do not satisfy the boundary conditions appropriate for networks. It has been shown that the theory of entanglement networks cannot be formulated in terms of junction positions and junction velocities alone as it has been done for isolated macromolecules and networks with localized junctions. Complete characterization of configurations in entangled systems requires (in addition to junction positions in Euclidean space) introduction of additional variables—distances measured along the contour of macromolecular chains. Limitations of the normal coordinate treatment in the application to localized and entanglement networks are discussed.

The aim of molecular considerations is to explain the origin, nature and mechanisms involved in physical phenomena rather than to reproduce experimentally established facts and relations. Therefore, every rational molecular theory should be derived from first principles, or based on independently determined, reliable physical information. A theory based on incorrect premises or one involving arbitrary, unjustified assumptions does not explain anything, and is meaningless even if it is made to fit some experimental data.

There exist molecular theories of dilute polymer solutions which, though based on rather simple molecular models, do explain the nature of viscoelasticity in such systems.[1,2] Similar theories exist also for permanent, ideal networks representing the equilibrium elasticity of rubbers.[3-5] No adequate molecular theory is available for the intermediate systems—concentrated polymer solutions, melts, and uncross-linked bulk polymers, however. The few consequent theoretical treatments[6-8] concern the molecular model ("temporary" network) which is incapable of describing many essential features of such systems; many other attempts are based on obscure premises and/or unjustified assumptions.

In early fifties several authors expressed the opinion that theories of dilute solutions can, after some modifications, be applied to condensed polymer systems.[9-11] The early model concepts however (*e.g.*, the "effective friction factor" for polymer melts,[10] arbitrarily assumed kinematics or dynamics of deformation[12-14]), were ill-defined, unverifiable and as such could not be subject to any serious analysis. On the other hand, during the recent 10 years appeared several papers which were to explain the viscoelastic behavior of network systems (regarded an appropriate model for concentrated solutions and bulk polymers) starting from the well defined concepts of the theory of dilute solutions.[11,15-20] Most of these theories considered kinematics of an isolated macromolecular chain. Such an approach is admissible for dilute solutions where the boundary conditions applied to the system are transmitted to every chain *via* a viscous continuum (solvent). In network systems the boundary conditions are transmitted to every network chain *via* other chains and the system should be considered as a whole unless admissibility of other approach is proved.

Kinematics and dynamics of chain macromolecules in network systems are fundamentally different from those in dilute solutions. Consequently, extension of the dilute solution theory to networks is inappropriate and illegitimate. The theory of networks should be based on considerations explicitly emphasizing chain-chain interactions in network junctions and the appropriate boundary conditions rather than on the modification of mobility of isolated macromolecules.

In many attempts at constructing molecular theories of concentrated polymer solutions the concepts derived from, and applicable to dilute solutions seem to be "absolutized" and implicitly assumed generally valid for any molecular system. We will discuss in this paper the fundamental differences in kinematics and dynamics of macromolecules in dilute solutions, on one hand, and in network systems, on the other one. We will show that, the "mobility matrices" appearing in the theory of Rouse[1] and Zimm[2] and used, after some modification, as a source of information about the relaxation time spectra for condensed polymer systems are irrelevant for macromolecules involved in network systems. It will also be demonstrated that the normal coordinate approach, so fruitful in the theory of dilute solutions, is not necessarily applicable to network systems.

In some papers[16,19] extension of the Rouse-Zimm theory is applied to what is called "entanglement systems." It will be shown that, because of the continuous variation of contour lengths between entanglement junctions (chain sliding), the theoretical language used in the theory of dilute solutions and involving only positions and velocities of friction centers (and network junctions) in a Euclidean space is absolutely inadequate for the theoretical analysis of entangled systems.

Kinematics and Dynamics of a Macromolecule in a Dilute Solution

We will repeat briefly the foundations of the theory of dilute solutions of flexible macromolecules. The theories of Rouse[1] and Zimm[2] use different languages but can be shown to be equivalent. We will follow the hydrodynamic language of Zimm[2] but its relation to the thermodynamic approach taken by Rouse[1] will be shown. For the sake of simplicity we will neglect hydrodynamic interactions between the individual parts of the macromolecule as well as the internal viscosity effects introduced by several other authors.

The macromolecule is represented by a system of N Gaussian subchains, or, what is equivalent, by a system of $(N + 1)$ friction centers (beads) connected by Hookean springs (Figure 1). In the coordinate system connected with the first bead the position of any ith bead is represented by a vector $\mathbf{r}^i$. External forces applied to the system are assumed to be transmitted to the macromolecule

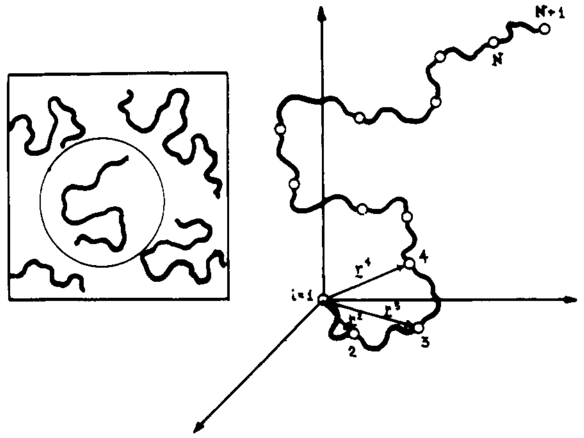

Figure 1. Model of a single chain-macromolecule in dilute solutions: open circles, friction centers.

as a frictional force *via* a viscous continuum (solvent) in which all macromolecules are embedded. It is also assumed that the velocity gradient in the solvent is a constant tensor **a** and, in the absence of hydrodynamic interactions, the velocity field in the solvent is identical around every bead.

The determining step in the theory is the formulation of the equation of motion. Consider the forces acting on some ith bead. They include:

(i) elastic tensions $\mathbf{f}_{\mathrm{el}}^{i-1,i}$ and $\mathbf{f}_{\mathrm{el}}^{i,i-1}$, due to intramolecular interactions of the ith bead with beads $i+1$ and $i-1$. With Gaussian statistics of conformations (or within the range of Hookean behavior of the springs)

$$\mathbf{f}_{\mathrm{el}}^{i+1,i} = (3kT/\langle h_0^2\rangle)(\mathbf{r}^{i+1} - \mathbf{r}^i) \qquad (1)$$

where $\langle h_0^2\rangle$ is the average square end-to-end distance for a single subchain at rest;

(ii) the "statistical" or "diffusional" force $\mathbf{f}_{\mathrm{dif}}^i$ acting on the ith bead when the spatial distribution of beads Ψ is nonuniform

$$\mathbf{f}_{\mathrm{dif}}^i = -kT\nabla_i \ln \Psi = -kT(\partial \ln \Psi/\partial \mathbf{r}^i) \qquad (2)$$

(iii) the external force transmitted from the boundary of the system and exerted on the ith bead by the solvent, $\mathbf{f}_{\mathrm{f}}^i$. In the first approximation (the Stokes' law), $\mathbf{f}_{\mathrm{f}}$ is proportional to the difference of velocities of the bead, $\dot{\mathbf{r}}^i$ and of the solvent surrounding this bead $\mathbf{v}(\mathbf{r}^i)$

$$\mathbf{f}_{\mathrm{f}}^i = -\zeta[\dot{\mathbf{r}}^i - \mathbf{v}(\mathbf{r}^i)] \qquad (3)$$

where $\zeta = \zeta_0 l_0$ is the molecular friction coefficient per subchain with a contour length l_0.

With the assumption of a constant velocity gradient **a**

$$\mathbf{v}(\mathbf{r}^i) = \mathbf{a}\mathbf{r}^i \qquad (4)$$

there results

$$\mathbf{f}_{\mathrm{f}}^i = -\zeta(\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i) \qquad (5)$$

The equation of motion at $\mathbf{r}^i$ (*i.e.*, for the ith bead)

$$m\ddot{\mathbf{r}}^i = \Sigma\mathbf{f}(\mathbf{r}^i) \qquad (6)$$

where m is mass and $\ddot{\mathbf{r}}^i$ acceleration of the ith bead, can thus be written in the form

$$m\ddot{\mathbf{r}}^i = \mathbf{f}_{\mathrm{el}}^{i+1,i} - \mathbf{f}_{\mathrm{el}}^{i,i-1} + \mathbf{f}_{\mathrm{dif}}^i + \mathbf{f}_{\mathrm{f}}^i \qquad (6a)$$

When acceleration $\ddot{\mathbf{r}}^i$ is negligible, and all force contributions written explicitly, eq 6 reduces to

$$(3kT/\langle h_0^2\rangle)(\mathbf{r}^{i+1} - 2\mathbf{r}^i + \mathbf{r}^{i-1}) - kT(\partial \ln \Psi/\partial \mathbf{r}^i) - \zeta(\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i) = 0 \qquad (7)$$

When the friction coefficient or the velocity difference is equal to zero, [$\zeta = 0$, or $(\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i) = 0$] as is the case when the system is at rest, two first terms of eq 7 determine the Gaussian distribution of all beads

$$\begin{aligned}\Psi_0 &= \text{const exp}\left[-3/(2\langle h_0^2\rangle)\sum_i(\mathbf{r}^i - \mathbf{r}^{i+1})^2\right] \\ &= \text{const exp}\left[-3/(2\langle h_0^2\rangle)\sum_i(\mathbf{h}^i)^2\right]\end{aligned} \qquad (8)$$

When the friction coefficient ζ is different from zero, eq 7 can be solved for the velocity difference $(\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i)$

$$\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i = -(3kT/\zeta\langle h_0^2\rangle)(-\mathbf{r}^{i+1} + 2\mathbf{r}^i - \mathbf{r}^{i-1}) - (kT/\zeta)\partial \ln \Psi/\partial \mathbf{r}^i \qquad (9a)$$

Rouse,[1] using local coordinates associated with individual subchains (vectors $\mathbf{h}^i$ instead of $\mathbf{r}^i$) and gradients of the chemical potential μ instead of elastic and diffusional forces, obtained the result

$$\dot{\mathbf{h}}^i - \mathbf{a}\mathbf{h}^i = -B[-\partial\mu/\partial\mathbf{h}^{i+1} + 2\partial\mu/\partial\mathbf{h}^i - \partial\mu/\partial\mathbf{h}^{i-1}] \qquad (9b)$$

where B is "mobility coefficient." It is easy to show that the transformation of coordinates

$$\mathbf{h}^i = \mathbf{r}^{i+1} - \mathbf{r}^i$$

and substitution

$$B = 1/\zeta$$

$$\mu = kT \ln (\Psi/\Psi_0) = kT\left[\ln \Psi + 3\sum_i(\mathbf{h}^i)^2/2\langle h_0^2\rangle\right] + \text{const} \qquad (10)$$

reduces the result of Rouse (eq 9b) exactly to the form of eq 9a derived by Zimm. Multiplying eq 9b by ζ and expressing it in an $(N+1)$-dimensional configuration space, one can write simply

$$\zeta(\dot{\mathbf{h}} - \mathbf{a}\mathbf{h}) = -\mathbf{A} \text{ grad } \mu \qquad (11)$$

where

$$\mathbf{h} = (\mathbf{h}^1, \mathbf{h}^2, \ldots, \mathbf{h}^{N+1})$$

$$\text{grad} = (\partial/\partial\mathbf{h}^1, \partial/\partial\mathbf{h}^2, \ldots, \partial/\partial\mathbf{h}^{N+1})$$

are vectors in the $(N+1)$-dimensional space, and **A** is the matrix

$$A_{ij} = \left\{\begin{array}{l} 1 \text{ for } i = j = 1 \text{ and } i = j = N+1 \\ -1 \text{ for } j = i-1 \text{ and } j = i+1 \\ 2 \text{ for } i = j \neq 1 \text{ and } i = j \neq N+1 \\ 0 \text{ for } j > i+1 \text{ and } j < i-1 \end{array}\right\} \qquad (12)$$

The matrix appearing in the theory of Rouse differs from that given by eq 12 in the terminal components

$$A_{11} = A_{N+1,N+1} = 2$$

Two conclusions, can be drawn out of eq 11.

$$\zeta = 0 \Longrightarrow \text{grad } \mu = 0 \Longleftrightarrow \Psi = \Psi_0 \qquad (13a)$$

$$\dot{\mathbf{h}} = \mathbf{a}\mathbf{h} \Longrightarrow \text{grad } \mu = 0 \Longleftrightarrow \Psi = \Psi_0 \qquad (13b)$$

If the friction coefficient ζ is equal to zero, or the chain deforms affinely (as does the solvent) the configuration distribution Ψ reduces to the fundamental form Ψ_0 (eq 8), and tensions in the individual subchains disappear. This conclusion corresponds with the well known fact, that dilute solutions cannot support any tension at equilibrium.

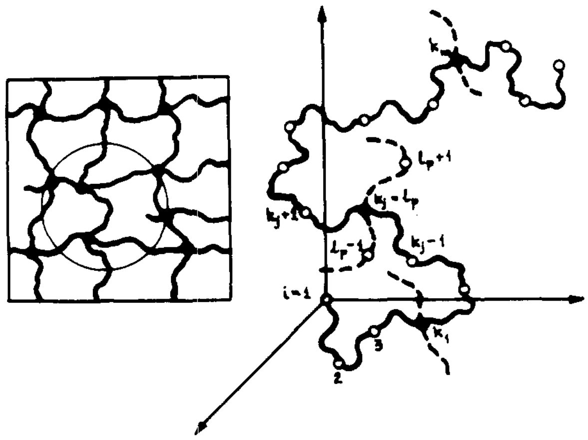

Figure 2. Model of a chain-macromolecule involved in a network system with localized junctions: open circles, friction centers between junctions; full circles, network junctions.

Modifications of the Rouse–Zimm theory for network systems involved first of all the form of the matrix **A** and/or the mobility coefficient B without changing the fundamental equations (9–11). It was postulated that, due to permanent, temporary, or "entanglement" junctions the mobility coefficient B and/or the matrix **A** for every single macromolecule should be changed and the modified mobility matrices were solved for eigenvalues subsequently identified with reciprocal relaxation times.[15,16,19] We will show below that mobility matrices for network systems are indeterminate and cannot serve as a source of information about the viscoelastic behavior.

Kinematics and Dynamics of a Linear Macromolecule Involved in a Network with Localized Junctions

Consider the model shown in Figure 2. A macromolecule consisting of $(N + 1)$ identical subchains (like that in Figure 1) is connected in m points (junctions)

$$i = k_1, k_2, \ldots, k_m$$

to other macromolecules, to form a coherent network. Positions of the junctions are shown by full circles. Open circles denote, as in Figure 1, the centers of friction resulting in polymer-solvent and polymer-polymer contacts. Separation of junctions along the chain (*i.e.*, the difference $k_j - k_{j-1}$) is not necessarily identical for all j. It should be emphasized that, while eq 6 is quite general (momentum conservation, or force balance equation), eq 6a–11 are specific forms of eq 6 valid for dilute solutions. Therefore, the theory of networks should not start from eq 6a–11 but force balance in all points of the macromolecular chain ($i = 1, 2, \ldots, N + 1$) should be analyzed with force contributions relevant for the given molecular system.

Consider first the friction centers, which are not network junctions, *i.e.*, $i \neq k_j$. Forces appearing in such points are identical with those discussed in the preceding section. With neglected inertial term we obtain:

$$\Sigma \mathbf{f} = \mathbf{f}_{\mathrm{el}}{}^{i+1,i} - \mathbf{f}_{\mathrm{el}}{}^{i,i-1} + \mathbf{f}_{\mathrm{dif}}{}^{i} + \mathbf{f}_{\mathrm{f}}{}^{i} = 0 \qquad (14)$$

It has been shown[21] that the frictional force $\mathbf{f}_{\mathrm{f}}{}^i$ for a subchain with contour length l_0 resulting from polymer-solvent and polymer-polymer contact interactions can be presented in the form

$$\mathbf{f}_{\mathrm{f}}{}^{i} = -Kl_0\Delta\mathbf{v}(\mathbf{r}^i) = -Kl_0[\dot{\mathbf{r}}^i - \mathbf{v}(\mathbf{r}^i)] \qquad (15)$$

where

$$K = \zeta_0(1 - v_{\mathrm{p}}) + \xi p(v_{\mathrm{p}})\cdot v_{\mathrm{p}} \qquad (16)$$

is the overall friction coefficient. ζ_0 in eq 16 denotes, as in dilute solutions, the polymer-solvent friction coefficient, ξ the polymer-polymer contact friction coefficient, p the number of polymer-polymer contacts per unit contour length, and v_p the volume fraction of polymer.

Using eq 4 for $\mathbf{v}(\mathbf{r}^i)$ we obtain for the friction centers the analog to eq 9a

$$Kl_0(\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i) = -(3kT/\langle h_0{}^2\rangle)[-\mathbf{r}^{i+1} + 2\mathbf{r}^i - \mathbf{r}^{i-1}] - kT\ \partial \ln \Psi/\partial \mathbf{r}^i \qquad (17)$$

Equation 17 is valid for nonterminal friction centers, *i.e.*, for $i \neq k_j$, $i \neq 1$, $i \neq N + 1$. For terminal centers (free chain ends) we have, as in dilute solutions,

$$Kl_0(\dot{\mathbf{r}}^1 - \mathbf{a}\mathbf{r}^1) = -(3kT/\langle h_0{}^2\rangle)[\mathbf{r}^1 - \mathbf{r}^2] - kT\ \partial \ln \Psi/\partial \mathbf{r}^1 \qquad (17a)$$

and

$$Kl_0(\dot{\mathbf{r}}^{N+1} - \mathbf{a}\mathbf{r}^{N+1}) = -(3kT/\langle h_0{}^2\rangle)[\mathbf{r}^{N+1} - \mathbf{r}^N] - kT\ \partial \ln \Psi/\partial \mathbf{r}^{N+1} \qquad (17b)$$

The situation is quite different, when the force balance in network junctions ($i = k_j$) is considered. In junction points (full circles in Figure 2) the elastic tensions of two subchains adjacent to the junction and originating from the macromolecule considered ($\mathbf{f}_{\mathrm{el}}{}^{k_j+1,k_j}$ and $\mathbf{f}_{\mathrm{el}}{}^{k_j,k_j-1}$) are balanced by frictional and diffusional terms ($\mathbf{f}_{\mathrm{f}}{}^{k_j}$ and $\mathbf{f}_{\mathrm{dif}}{}^{k_j}$, respectively) together with elastic and diffusional terms associated with two other subchains connected to the junction and originating from a different macromolecule (one drawn in dashed line in Figure 2). If, in the coordinate system associated with this other macromolecule our junction point (k_j) has index (l_p) and the position $\tilde{\mathbf{r}}^{l_p}$, in the force balance equation will appear additional elastic tensions $\mathbf{f}_{\mathrm{el}}{}^{l_p+1,l_p}$ and $\mathbf{f}_{\mathrm{el}}{}^{l_p,l_p-1}$ and an additional diffusional term $\mathbf{f}_{\mathrm{dif}}{}^{l_p}$, all associated with the other macromolecule

$$\Sigma \mathbf{f} = \mathbf{f}_{\mathrm{el}}{}^{k_j+1,k_j} - \mathbf{f}_{\mathrm{el}}{}^{k_j,k_j-1} + \mathbf{f}_{\mathrm{el}}{}^{l_p+1,l_p} - \mathbf{f}_{\mathrm{el}}{}^{l_p,l_p-1} + \mathbf{f}_{\mathrm{f}}{}^{k_j} + \mathbf{f}_{\mathrm{dif}}{}^{k_j} + \mathbf{f}_{\mathrm{dif}}{}^{l_p} = 0 \qquad (18)$$

Equation 18 with all force contributions written explicitly, when solved for velocity difference yields, instead of eq 17 or 7

$$Kl_0(\dot{\mathbf{r}}^{k_j} - \mathbf{a}\mathbf{r}^{k_j}) = -(3kT/\langle h_0{}^2\rangle)[-\mathbf{r}^{k_j+1} + 2\mathbf{r}^{k_j} - \mathbf{r}^{k_j-1} - \tilde{\mathbf{r}}^{l_p+1} + 2\tilde{\mathbf{r}}^{l_p} - \tilde{\mathbf{r}}^{l_p-1}] - kT(\partial \ln \Psi/\partial \mathbf{r}^{k_j} + \partial \ln \Psi/\partial \tilde{\mathbf{r}}^{l_p}) \qquad (18a)$$

or, in the language of Rouse

$$Kl_0(\dot{\mathbf{h}}^{k_j} - \mathbf{a}\mathbf{h}^{k_j}) = -(-\partial\mu/\partial\mathbf{h}^{k_j+1} + 2\partial\mu/\partial\mathbf{h}^{k_j} - \partial\mu/\partial\mathbf{h}^{k_j-1}) - (-\partial\mu/\partial\tilde{\mathbf{h}}^{l_p+1} + 2\partial\mu/\partial\tilde{\mathbf{h}}^{l_p} - \partial\mu/\partial\tilde{\mathbf{h}}^{l_p-1}) \qquad (18b)$$

Comparing eq 18a and 18b with corresponding equations of the theory of dilute solutions (eq 9a and 9b), one can observe that in the kinematics of network junctions appear not only positions and distribution gradients of the macromolecule considered (characteristics with indices k_j, $k_j + 1$, $k_j - 1$) but also coordinates and gradients concerning the other macromolecule participating in the formation of the junction (characteristics with indices l_p, $l_p + 1$, $l_p - 1$). In eq 18a,b appear positions of segments belonging to two different macromolecules and expressed in two different coordinate systems ($\mathbf{r}^i$ and $\tilde{\mathbf{r}}^m$); the distribution function Ψ and the chemical potential μ depend simultaneously on $\mathbf{r}^i$ and $\tilde{\mathbf{r}}^m$ (or $\mathbf{h}^i$ and $\tilde{\mathbf{h}}^m$). Characteristics of two macromolecules contacting in the jth junction cannot inherently be expressed in the language describing a

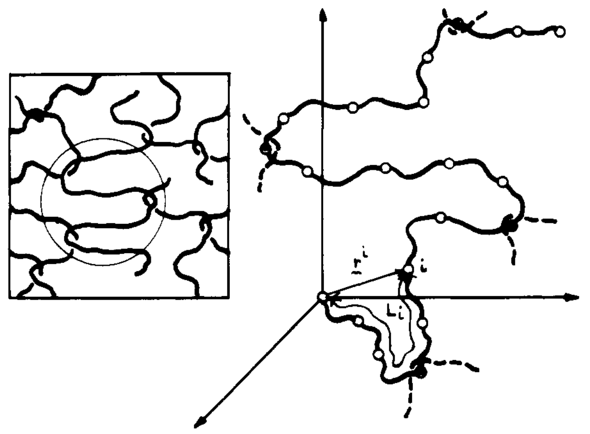

Figure 3. Model of a chain-macromolecule involved in an entanglement network: open circles, friction centers; open circles with central dots, entanglement points.

single macromolecule. Equations 18a,b cannot be solved for velocity difference and do not provide any information about the kinematics of the junction. Consequently, there does not exist any unique relation between positions of the individual points of the considered macromolecule, $\mathbf{r}^i$ or between gradients of its chemical potential $\partial\mu/\partial\mathbf{h}$, on one hand, and velocities ($\dot{\mathbf{r}}^i$, or $\dot{\mathbf{h}}^i$), on the other hand. Therefore the "mobility matrix" for a single macromolecule involved in a network cannot be formulated and all attempts of describing the kinematics of networks in terms of such matrices[15-17] are incorrect in principle. On the other hand, the error involved in the work of Forsman and Grand[19] consists in identification of two different gradients of the distribution function Ψ: $\partial \ln \Psi/\partial\mathbf{r}^i$ (gradient with respect to the coordinates $\mathbf{r}^i$ of the considered macromolecule) and $\partial \ln \Psi/\partial\tilde{\mathbf{r}}^m$ related to the coordinates of the other macromolecule which interacts with the first one in the junction point. This incorrect identification brought Forsman and Grand to results very similar to those obtained by Chömpff and Duiser.[15,16]

We will show now that the effects exerted on the junction point of the considered macromolecule by subchains of the other molecule (in eq 18a,b all terms with indices l_p, $l_p + 1$, $l_p - 1$) cannot be approximated by a mere modification of the "mobility" of the junction point, as suggested by Chömpff and Duiser. To prove this point, we will compare eq 18b with a modified equation of Rouse (eq 7) in which the junction point ($i = k_j$) has "mobility" modified by a factor δ

$$Kl_0(\dot{\mathbf{h}}^{k_j} - \mathbf{a}\mathbf{h}^{k_j}) = -\delta(-\partial\mu/\partial\mathbf{h}^{k_j+1} + 2\partial\mu/\partial\mathbf{h}^{k_j} - \partial\mu/\partial\mathbf{h}^{k_j-1}) \quad (19)$$

The hypothetical eq 19 seems to reflect correctly the leading idea of the theories criticized above.[15-17]

Assume that the system is kept at constant, but nonzero deformation, so that $\mathbf{a} = 0$ and all $\dot{\mathbf{h}} = 0$. With left-hand side equal to zero, eq 19 yields

$$\mathbf{a} = 0 \Longrightarrow \text{grad } \mu = 0 \Longleftrightarrow \Psi = \Psi_0 \quad (20)$$

Equation 20 describes behavior typical for dilute solutions—no tensions when the system is at rest. Such a prediction is unphysical for networks which are known to support tensions when kept at constant deformation; equilibrium tensions should appear in permanently cross-linked networks, time-dependent (relaxing) tensions in "temporary" systems.

On the other hand, from our eq 18b derived for a network at $\mathbf{a} = 0$ results a definite relation between the gradients of the chemical potential μ taken with respect to coordinates of two different macromolecules

$$\partial\mu/\partial\mathbf{h}^{k_j+1} - 2\partial\mu/\partial\mathbf{h}^{k_j} + \partial\mu/\partial\mathbf{h}^{k_j-1} = -(\partial\mu/\partial\tilde{\mathbf{h}}^{l_p+1} - 2\partial\mu/\partial\tilde{\mathbf{h}}^{l_p} + \partial\mu/\partial\tilde{\mathbf{h}}^{l_p-1}) \quad (21)$$

Equation 21 does not imply that the distribution function Ψ is a product of two fundamental functions Ψ_0, or that any one of the gradients $\partial\mu/\partial\mathbf{h}^i$, or $\partial\mu/\partial\tilde{\mathbf{h}}^m$ is equal to zero.

$$\partial\mu/\partial\mathbf{h}^i \neq 0, \partial\mu/\partial\tilde{\mathbf{h}}^m \neq 0$$
$$\Psi(\mathbf{h}^i, \tilde{\mathbf{h}}^m) \neq \Psi_0(\mathbf{h}^i)\Psi_0(\tilde{\mathbf{h}}^m)$$

Analysis of eq 20 shows that the model of "modified mobility" does not in fact predict any network behavior. On the other hand, the correct force balance equation (eq 18b) yields a result (eq 21) which is consistent with fundamental properties of network systems.

There is also another important condition which should be satisfied in networks but cannot be realized in the modified Rouse–Zimm approach. Continuity of any network system stipulates that all network chains deform in the average like the boundary of the system. There is no such requirement in systems containing isolated macromolecules. Dilute solutions assume unlimited deformations as a whole, while accompanied by small and always finite deformations of structural elements (subchains). Kinematic solutions based on the original (eq 9a,b) or the modified Rouse–Zimm equations (eq 19) do not satisfy the appropriate boundary conditions for networks and are inapplicable to such systems.

It has been shown that the equation of motion for networks (eq 18a or 18b) derived in the same way as it had been done in the theory of dilute solutions cannot be solved for kinematic characteristics (junction velocities) $\dot{\mathbf{r}}$ or $\dot{\mathbf{h}}$. Some information about these characteristics can be obtained from thermodynamic considerations.

For ideal, permanently cross-linked systems composed of Gaussian chains, it has been found[22,23] that thermodynamically most probable displacement of all junctions is affine, *i.e.*, satisfies the condition

$$\dot{\mathbf{r}}^i = \mathbf{a}\mathbf{r}^i \quad \text{for all } i \quad (22)$$

It is obvious that eq 22 satisfies the boundary condition: all network chains displace identically and in the same way as does boundary of the system. Equation 22 has subsequently been assumed in the models of "temporary" networks by Yamamoto and Lodge[7,8] where no polymer-solvent or polymer-polymer friction was taken into account.

It can be shown[24] that the affine displacement of all network junctions (eq 22) minimizes simultaneously the total energy of the network and the dissipated energy, provided that network chains are Gaussian (or deformations are small), internal viscosity of chains is negligible and no entrapped entanglements are present in the system. Hence eq 22 provides a reasonable solution of the kinematic problem for all networks with localized junctions (permanent or temporary). When network chains are non-Gaussian, exhibit high internal viscosity, or the system is entangled, eq 22 is no more applicable and the kinematic problem remains unsolved.

The kinematics involved in eq 22 can also be used in the evaluation of the model proposed by Mooney[11] and developed recently by Ilavsky *et al.*[18] Mooney considered a single macromolecule participating in a rubber network with frictional interactions between network chains. The macromolecule was assumed to be deformed instantaneously, so that its initial configuration was far from equilibrium; the relaxation of stress following such a deformation was to result from the gradual rearrangement of molecular configuration toward most probable (equilibrium) state. In the light of the thermodynamic sense of the affinity condition (eq 22) the model appears to be unrealizable. If the system is actually a network, with polymer–polymer (or even polymer–solvent) contact interactions, its instantaneous deformation, and the more so, one leading to molecular configurations far from equilibrium, is impossible. Instantaneous deformations of a viscoelastic body require infinite stresses; most probable deformation of the system and every macromolecule would be affine (eq 22) corresponding to zero dissipation and most probable (equilibrium) molecular configuration. Such deformation, however, would not be followed by any molecular arrangement and any relaxation of stress.

Networks with Localized Junctions *vs.* Entanglement Networks

The model of a "temporary" network with localized junctions has originally been proposed for chemically crosslinked systems with high but finite bond energy ("chemical" relaxation of rubbers).[6] More recent developments of this model[7,8] recommended its application to concentrated polymer solutions and melts. There is one point however which makes networks with localized junctions inherently incapable of describing the mechanical properties of condensed polymer fluids.

In the theory of localized networks does not appear molecular weight of the primary (uncross-linked) macromolecules; all the physical characteristics of such systems are determined by molecular weights of network chains, *i.e.*, of the sections of primary macromolecules included between adjacent network junctions. On the other hand, it is well known that mechanical properties of dense polymer fluids are very sensitive to the primary molecular weight of the dissolved or molten polymer (*cf.* the empirical "3.4 power law" in viscosity). This inherent inability of the model to account for molecular weight effects excludes its application to polymer solutions and melts and reduces its use to chemically cross-linked systems with weak chemical bonds, like rubbers and strongly polar gels.

The model free of such a limitation is provided by an entanglement network. Junctions in such a network are not localized and can slide continuously along macromolecular chains. Primary macromolecules do not lose their individuality when joining the network (as was the case with localized networks) and the effects of primary molecular weight can be expressed strongly.

Theoretical treatment of entanglement systems cannot be based on the positions and velocities of junctions in a three-dimensional Euclidean space that was sufficient for isolated macromolecules and networks with localized junctions.

Besides the positions of junctions (or friction centers) in this space (vectors $\mathbf{r}^i$ or $\mathbf{h}^i$) one should consider also other configuration characteristics, *viz.*, positions in the space of the macromolecule, *i.e.*, distances from the free chain end, L^i, or from the adjacent junction $l^i = L_{i-1} - L_i$ measured along the contour of the chain (*cf.* Figure 3). Therefore the complete characteristic of an entanglement point involves four coordinates (x^i, y^i, z^i, L_i) rather than three (x^i, y^i, z^i) sufficient for the treatment of dilute solutions, and the configuration space for the system consisting of N elements is therefore $4N$-dimensional, rather than $3N$-dimensional. Similarly, the kinematics of entangled systems involve four velocity components for each point ($\dot{\mathbf{r}}^i$ and $\dot{L}_i$ or $\dot{\mathbf{h}}^i$ and $\dot{l}_i$).

Many authors use the term "entanglement" without specification of its exact meaning and without explicit formulation of its configuration and kinematics.[12,14,16,25] In some papers (*e.g.*,[19,25,26]) "entanglements" are considered just additional network junctions equivalent to localized (permanent or temporary) cross-links. In view of the fundamental difference in kinematic and dynamic behavior of entanglements as compared with localized junctions, such approach is incorrect and the systems discussed in the above papers are, in fact, no entanglement systems. Whatsoever is the detailed geometrical definition of an entanglement, variable contour lengths (L, l) and continuous chain sliding are fundamental features of all entanglement systems and cannot be neglected in any theoretical treatment. To show the kinematic and dynamic differences between entanglement and localized networks, we will analyze the equation of motion for an entangled macromolecule along the same lines as it has been done for dilute solutions and localized networks.

Kinematics and Dynamics of a Macromolecule Involved in an Entanglement Network

Figure 3 presents a macromolecule consisting of $N + 1$ subchains involved in an entanglement network. Positions of the individual friction centers are marked by open circles, and positions of m entanglement junctions by circles with central dots. Coordinates of the end of an ith subchain are $\mathbf{r}^i$ (the distance from the origin of the coordinate system placed at the chain end), and $L_i = il_0$ (contour length of the macromolecule measured from the chain end up to the ith terminating point). l_0 is (equal for all subchains) the contour length of a single subchain.

Coordinates of any jth junction ($j = 1, 2, \ldots, m$) are $\mathbf{r}^{k_j}$, $L_{k_j} = k_j l_0$, where k_j are not necessarily uniformly distributed along the chain.

The rate of chain sliding, *i.e.*, variation of the contour lengths ($\dot{L}$, or $\dot{l}$) affects the actual velocity difference $\Delta\mathbf{v}$ in polymer–polymer or polymer–solvent contacts and therefore also the effective contact friction $\mathbf{f}_f$. Extending the analysis included in ref 21, one obtains the effective velocity difference in some ith friction center with coordinates ($\mathbf{r}^i$, L_i) included between the jth and (j + 1)-st entanglement junctions, in the form

$$\Delta\mathbf{v}(\mathbf{r}^i) = \dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i - [\dot{L}_{k_j} + (L_i - L_{k_j})(\dot{L}_{k_{j+1}} - \dot{L}_{k_j})/(L_{k_{j+1}} - L_{k_j})](\mathbf{r}^{k_{j+1}} - \mathbf{r}^{k_j})/(L_{k_{j+1}} - L_{k_j}) \quad (23)$$

where

$$k_j < i < k_{j+1}$$

and the differences $(\mathbf{r}^{k_{j+1}} - \mathbf{r}^{k_j}) = \mathbf{h}^j$, and $(L_{k_{j+1}} - L_{k_j}) = l_j$ represent respectively the end-to-end vector and the contour length of jth network chain, included between the entanglements j and $j + 1$.

The friction force corresponding to eq 23 differs from that calculated from eq 15. The additional terms are associated with chain sliding and disappear when all contour lengths L_i are constants, or sliding rates $\dot{L}_i$ are equal to zero. In the presence of chain sliding however ($\dot{L} \neq 0$) the velocity difference does not disappear even when deformations are affine, *i.e.*, when $\dot{\mathbf{r}}^i = \mathbf{a}\mathbf{r}^i$.

Force balance for any ith friction center (*i.e.*, the point not involved directly in any entanglement junction, $i \neq k_j$) results, like in the models discussed before, from elastic tensions of two adjacent subchains, a diffusional contribution and contact friction $\mathbf{f}_f$, the last term completed with chain sliding effects (eq 23)

$$\dot{\mathbf{r}}^i - \mathbf{a}\mathbf{r}^i = -(3kT/\langle h_0^2\rangle Kl_0)[-\mathbf{r}^{i+1} + 2\mathbf{r}^i - \mathbf{r}^{i-1}] - (kT/Kl_0)(\partial \ln \Psi/\partial \mathbf{r}^i) + [\dot{L}_{k_j} + (L_i - L_{k_j})(\dot{L}_{k_{j+1}} - \dot{L}_{k_j})/(L_{k_{j+1}} - L_{k_j})](\mathbf{r}^{k_{j+1}} - \mathbf{r}^{k_j})/(L_{k_{j+1}} - L_{k_j}) \quad (24)$$

It can be observed, that, unlike in eq 9 or 17, velocity difference in a friction center can be found from the equation of motion only when some independent information about the contour lengths L and sliding rates $\dot{L}$ is available.

Force balance in an entanglement junction ($i = k_j$) is even more complex, since in addition to the elastic tensions of two different pairs of subchains entangled in the point k_j and corresponding diffusional contributions there appears also friction in the entanglement point, controlled by sliding rates of both macromolecules.[21] Application of the mobility matrices is excluded even for the sections of macromolecule between entanglements ($i \neq k_j$). So, the dilute solution approach fails also when applied to entanglement networks. At the same time it can be shown that affine deformations of entanglement points (eq 22) do not minimize free energy of the system, even so, when ideally flexible and Gaussian chains are considered.[24] Detailed kinematics of entanglement networks (*i.e.*, junction velocities, $\dot{\mathbf{r}}$ and sliding rates $\dot{L}$) should be found before any further information about the mechanical behavior is derived. Neither in the early papers concerning entanglement systems[12,14] nor in more recent publications[16,19,25] has an attempt been made to solve this problem.

Applicability of the Normal Coordinates Approach to Network Systems

Linear transformation of coordinates leading to so-called "normal modes" of chain deformation has proved to be very fruitful in the theory of dilute polymer solutions.[1,2] We will show that application of this approach is limited and not always can be extended onto network systems.

Consider the equation of continuity. For isolated macromolecules (dilute solutions) or networks with localized junctions (permanent, or temporary), the configurational space is $3N$-dimensional, the configuration characteristics being positions, $\mathbf{r}^i$ (or end-to-end vectors $\mathbf{h}^i$), of N subchains (network chains). By

$$\mathbf{h} = (\mathbf{h}^1, \mathbf{h}^2, ..., \mathbf{h}^N)$$

we will understand the $3N$-dimensional vector describing simultaneous position of all N subchains of a macromolecule. The equation of continuity in $3N$-dimensional space can thus be written in the form

$$\partial\Psi/\partial t + \partial^T(\Psi\dot{\mathbf{h}})/\partial\mathbf{h} = \begin{cases} 0 & \text{dilute solutions,} \quad (25\text{a}) \\ & \text{permanent networks} \\ \dot{\Psi}_{\text{kin}}(\Psi, \dot{\mathbf{h}}, \mathbf{h}) & \text{temporary networks} \quad (25\text{b}) \end{cases}$$

Ψ ($\mathbf{h}$, t) is the distribution density function in the $3N$-dimensional space and $\dot{\Psi}_{\text{kin}}$ is the kinetic term, *i.e.*, the net rate of formation of macromolecules with a given configuration. For dilute solutions and permanent networks where no junctions dissociate or are formed, $\dot{\Psi}_{\text{kin}}$ is equal to zero; for temporary networks, the kinetic term should be taken into account.

For entanglement systems, the configuration characteristics involve network chain vectors $\mathbf{h}$ and contour lengths, $\mathbf{l}$

$$\mathbf{h} = (\mathbf{h}^1, \mathbf{h}^2, ..., \mathbf{h}^N)$$
$$\mathbf{l} = (\mathbf{l}_1, \mathbf{l}_2, ..., \mathbf{l}_N)$$

and the kinematic characteristics include junction velocities $\dot{\mathbf{h}}$ and chain sliding rates $\dot{\mathbf{l}}$. Consequently, the time-dependent distribution function $\Psi^*(\mathbf{h}, \mathbf{l}, t)$ will be defined as the probability density in $4N$-dimensional space and the equation of continuity will assume the form

$$\partial\Psi^*/\partial t + \partial^T(\Psi^*\dot{\mathbf{h}})/\partial\mathbf{h} + \partial^T(\Psi^*\dot{\mathbf{l}})/\partial\mathbf{l} = \dot{\Psi}_{\text{kin}}{}^*(\Psi^*, \dot{\mathbf{h}}, \dot{\mathbf{l}}, \mathbf{h}, \mathbf{l}) \quad (26)$$

In the case of dilute solutions, there does exist a linear transformation of positions $\mathbf{h}$ into velocities $\dot{\mathbf{h}}$. From eq 9b

$$\dot{\mathbf{h}}^i = \mathbf{a}\mathbf{h}^i - BA_{ij}(\partial\mu/\partial\mathbf{h}^j) = \mathbf{a}\mathbf{h}^i - BkTA_{ij}(3\mathbf{h}^j/\langle h_0^2\rangle + \partial \ln \Psi/\partial\mathbf{h}^j) \quad (27)$$

With $\dot{\mathbf{h}}$ from eq 27 and after application of the orthogonal transformation of coordinates Q

$$\mathbf{h} \longrightarrow \mathbf{Q}\eta$$

which brings the matrix $\mathbf{A}$ into the diagonal form $\mathbf{M}$ eq 25a reduces to the "normal" form

$$\partial\Psi/\partial t + \partial^T[\Psi\mathbf{a}\eta - (3kTB/\langle h_0^2\rangle)\Psi\mathbf{M}\eta - kTB\mathbf{M}(\partial\Psi/\partial\eta)]/\partial\eta = 0 \quad (28)$$

We will investigate the possibility of a similar transformation of eq 25b and 26. The first difficulty may arise from the right-hand term, $\dot{\Psi}_{\text{kin}}$, or $\dot{\Psi}_{\text{kin}}{}^*$. Assume for a while that $\dot{\Psi}_{\text{kin}}$ is invariant *vs.* transformation of coordinates, and consider the temporary network with localized junctions (eq 25b). In the range of Gaussian statistics and in the absence of internal viscosity, the velocity $\dot{\mathbf{h}}$ is affine (eq 22) and eq 25b reduces automatically to the "normal form" without any transformation

$$\partial\Psi/\partial t + \partial^T(\Psi\mathbf{a}\mathbf{h})/\partial\mathbf{h} = \dot{\Psi}_{\text{kin}} \quad (29)$$

Equation 29 which is the result obtained in[7,8] does not involve any explicit spectrum of relaxation times. The only mechanism of dissipation is associated with the kinetic term $\dot{\Psi}_{\text{kin}}$, rather than any modes of chain deformation.

Consider now entanglement networks. Put aside the problem of the kinetic term $\dot{\Psi}_{\text{kin}}{}^*$ and assume that both kinematic characteristics, $\dot{\mathbf{h}}$ and $\dot{\mathbf{l}}$ can be expressed as linear transformations of the positions, and gradients of the distribution function Ψ^*

$$\dot{\mathbf{h}}^i = \mathbf{a}\mathbf{h}^i + C_{ij}\mathbf{h}^j + (aC_{ij} + b\delta_{ij})(\partial \ln \Psi^*/\partial\mathbf{h}^j)$$
$$\dot{l}_i = D^{ij}l_j \quad (30)$$

where a and b are constants. With $\dot{\mathbf{h}}$ and $\dot{\mathbf{l}}$ from eq 30, the equation of continuity (eq 26) reads

$$\partial\Psi^*/\partial t + \partial^T[\Psi^*\mathbf{a}\mathbf{h} + \Psi^*\mathbf{C}\mathbf{h} + (a\mathbf{C} + b\mathbf{I})(\partial\Psi^*/\partial\mathbf{h})]/\partial\mathbf{h} + \partial^T(\Psi^*\mathbf{D}\mathbf{l})/\partial\mathbf{l} = \dot{\Psi}_{\text{kin}}{}^* \quad (31)$$

where $\mathbf{I}$ is the unit transformation.

Orthogonal transformations of coordinates $\mathbf{h}$ and $\mathbf{l}$

$$\mathbf{h} \longrightarrow \mathbf{Q}\eta$$
$$\mathbf{l} \longrightarrow \mathbf{S}\lambda$$

such, that bring matrices $\mathbf{C}$ and $\mathbf{D}$ to diagonal forms ($\mathbf{M}$ and $\mathbf{N}$, respectively) yield again the "normal" form of the continuity equation

$$\partial\Psi^*/\partial t + \partial^T[\Psi^*\mathbf{a}\eta + \Psi^*\mathbf{M}\eta + (a\mathbf{M} + b\mathbf{I})(\partial\Psi^*/\partial\eta)]/\partial\eta + \partial^T(\Psi^*\mathbf{N}\lambda)/\partial\lambda = \dot{\Psi}_{\text{kin}}{}^* \quad (32)$$

This procedure is effective, and normalization of coordinates possible, when the kinematic characteristics $\dot{\mathbf{h}}$ and $\dot{\mathbf{l}}$ can be presented as linear transformations of the respective configuration variables $\mathbf{h}$ and $\mathbf{l}$ (eq 30) and when the corresponding matrices ($\mathbf{C}$, $\mathbf{D}$) are symmetrical. In fact, the kinematics of entanglement networks is more complex; as evident from eq 23, the velocity of friction centers, $\dot{\mathbf{r}}$, depends not only on the positions $\mathbf{r}$ but also on the sliding rates $\dot{L}_j$ and contour lengths L_j and cannot be reduced to linear relations assumed in eq 30. The same can be said about the other kinematic characteristic, $\dot{\mathbf{l}}$. Consequently, it cannot be shown what transformation would bring the problem to the "normal" form. It is not excluded though that some special cases of entanglement networks can still be described in terms of normal coordinates.

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Conformational and Packing Stability of Crystalline Polymers. IV. Polyethers $[\text{-O(CH}_2)_m\text{-}]_n$ and Polythioethers $[\text{-S(CH}_2)_m\text{-}]_n$ with $m = 2$ and 3

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ABSTRACT: Energy calculations covering both the helical and glide-type conformations have been derived, the planar zigzag being the special case of both these conformations. For the calculation, the intramolecular potential energy due to the internal rotation barriers, van der Waals interactions, and electrostatic interactions were taken into account. The stable conformations of polyethers $[\text{-O(CH}_2)_m\text{-}]_n$ with $m = 2$ and 3, *i.e.*, poly(ethylene oxide) (PEO) and polyoxacyclobutane (POCB), and polythioethers $[\text{-S(CH}_2)_m\text{-}]_n$ with $m = 2$ and 3, *i.e.*, poly(ethylene sulfide) (PES) and poly(trimethylene sulfide) (PTMS), were analyzed. According to the results of the calculations, the two modifications of PEO ((7/2) helix and planar zigzag), the conformation of PEO molecule in mercuric chloride complex type II, the three modifications of POCB (planar zigzag, glide type, and helix), and the conformations of the polythioethers, PES (glide type), and PTMS (G_4 type) were well explained. The intermolecular interaction energies in crystal for PEO, POCB, and PES were also calculated and discussed.

In a previous paper[1] of this series, the most stable conformations of several isotactic helical polymers were studied based upon the results of intramolecular energy calculations. The present study is an extention of this previous work and covers both helical and glide-type conformations, the planar zigzag being the special case of these conformations. The stable conformations of the polyethers $[\text{-O(CH}_2)_m\text{-}]_n$ with $m = 2$ and 3, *i.e.*, poly(ethylene oxide) (PEO) and polyoxacyclobutane (POCB), and polythioethers $[\text{-S(CH}_2)_m\text{-}]_n$ with $m = 2$ and 3, *i.e.*, poly(ethylene sulfide) (PES) and poly(trimethylene sulfide) (PTMS), were analyzed by this method and the results for polyethers were compared with those of corresponding polythioethers.

The conformational energy calculation under helical symmetry for PEO was reported by Magnasco *et al.*,[2] but such work as energy calculations covering both helical and glide-type conformations for these polyethers and polythioethers has not yet been reported.

Methods and Assumptions

Helical Conformations. In the case of the helical conformations, the energy calculations were made according to the same method described in the second paper[1] of this series; the fiber identity period was not fixed and it was only assumed that the chain forms a helical structure, *i.e.*, the set of the internal rotation angles repeats along the chain.

Glide-Type Conformation. For the glide-type conformations, the following two conditions are necessary:[3] (a) the signs of the corresponding internal rotation angles of the neighboring structural units are reversed, and (b) a translational unit consists of two structural units. The polymer chain having glide symmetry is shown as follows: