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Transient Network Theory for Shear-Thickening Fluids and Physically Cross-Linked Systems

Shi-Qing Wang

Departments of Macromolecular Science and Physics, Case Western Reserve University, Cleveland, Ohio 44106

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ABSTRACT: A model is introduced to treat the dynamics of coexistence between a physically cross-linked network with temporary junctions and unbound chains. Focusing on unentangled networks in which the molecular weight between neighboring cross-links is smaller than the entanglement molecular weight, we introduce three types of chains in a network-forming system: the elastically effective chains in the network that undergo affine deformation, dangling chains with one end sticking to junctions that experience deformation only through viscous interactions, and unbound free chains. Kinetic exchange between these chains is described by deriving three rate equations. The condition of incompressibility allows us to solve these coupled equations for arbitrary macrodeformation. Under deformations that are invariant in time, we obtain explicit expressions for the steady-state number density of each type of chain, exchange rates between different chains, steady-state shear viscosity, and normal stress differences. This study, besides representing an important extension of previous transient network models, provides a theoretical basis for explaining shear-thickening phenomena in certain gellike systems.

I. Introduction

Recently shear-thickening phenomena have drawn much interest from the scientific community of complex fluids including polymers and colloids. Both associating polymers such as ionomers[1,2] and charged micelles[3,4] display peculiar rheological behaviors such as shear thickening[1] and extraordinarily slow stress growth.[4] Simple qualitative arguments[4] have been provided to suggest formation of large clusters or aggregates for micelles under the influence of shear flow. For associating polymers, Witten and Cohen[5,6] argued that shear flow would help convert intrachain pairings between functional groups to interchain pairings and induce formation of networklike structures, causing the shear viscosity to increase over its low-shear Newtonian value. However, no analytical theories have been developed to quantify these experimental observations. Progress in our theoretical understanding of this class of solutions is hindered by the lack of knowledge concerning what and how microscopic processes lead to creation and annihilation of junctions among constituent particles.[6,7] Interchain junctions are certainly possible for polymers with associating functional groups when chains find themselves near one another in space. It is less clear how these junctions would exist among charged micelles that have no specific interacting groups. Of course, micelles can become attractive just like any other colloidal particles if they have overcome the electric double-layer repulsion to come very close to each other. Long flexible micelles in moderate concentrations can also form entanglements that act like temporary cross-links. Here we are content to assumed that in shear-thickening systems such junctions can be produced with a lifetime much longer than the relaxation times of individual chains and network structures resulting from these junctions are responsible for novel rheological properties.

Existing transient network models are designed to describe polymeric systems with temporary junctions. Allowing creation and annihilation of cross-links during deformation, Green and Tobolsky[8] extended classical rubber elasticity theories to model polymeric liquids as having a rubberlike network that is not formed by chemical bonds but by entanglements or weak breakable bonds such as hydrogen bonds. Thus by construction, such networks are capable of flowing upon deformation in contrast to a premanently cross-linked network. Later Lodge[9] introduced multiple relaxation processes into the Green–Tobolsky (GT) model to predict many of the qualitative phenomena of viscoelastic flow. At the same time Yamamoto[10] generalized the GT model by considering a dependence of junction breakage probability on chain conformation. To depict re-formation of entanglements in polymer melts, Yamamoto also kept a generation function for junctions. Due to the lack of molecular-level knowledge of entanglement dynamics, the generation junction remained somewhat arbitrary and difficult to be specified. One of the most recent studies on transient network theories is that of Tanaka and Edwards (TE).[11] In the TE theory, the Yamamoto model for the dynamics of entangled polymer melts[10] was modified to describe thermoreversible networks (or physical gels) comprised of chains with two functional groups on each end. Because of conservation of chains, TE arrived at a generation function for cross-linking at time t that itself depends on the number of cross-links at t. It is important to note that all the transient network theories mentioned above have one feature in common; i.e., there exist no unconstrained free chains and no kinetic exchange between networked chains and free ones. Our considerabion of a transient network in equilibrium with unbound chains, besides being an important extension of the previous studies on transient networks, is motivated by two practical situations as described below.

If associating polymer or micellar chains form a transient network in solution with no free chains in the quiescent state, then a shear flow field acts only to deform the network and to tear it apart at high shear by producing *free* chains. This leads to shear thinning and is what happens at high concentrations. To describe this strong flow case, we need to consider a balance between the network and free chains removed from the former by flow. At lower concentrations, such solutions are Newtonian for weak shear and become shear-thickening before turning shear-thinning with increasing shear rate γ. What causes shear thickening? It is plausible that a transient network or large clusters of chains coexist in equilibrium with free chains in these moderately concentrated solutions. Shear flow induces coagulation between free chains and the preexisting network, producing more junctions than in

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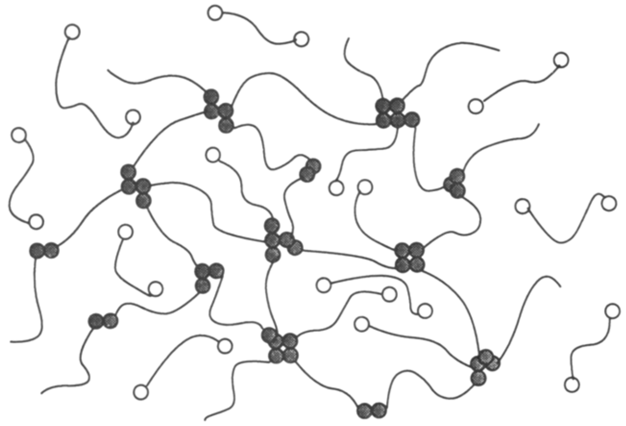

Figure 1. Schematic representation of a transient network made up of effective, free, and dangling chains. The dangling end is indicated by the open circle.

equilibrium. Due to this shear-enhanced gelation large networklike structures form to produce unusually high stress to be reflected in shear thickening. Therefore to develop a systematic theory for dynamics and rheology of shear-thickening fluids, we need to generalize existing transient network models.

In weakly physically cross-linked gels or slightly entangled concentrated polymer solutions, we may assume that not all the polymer chains participate in networking or clustering. A fraction of chains is individually suspended free chains. The *long* time (low frequency, low shear rate) response of such a system to externally imposed deformation is the action of *constrained* chains forming the transient networks. The high frequency and shear rate properties are determined by individual chains including free chains. Viscoelastic properties and rheological behaviors of such systems cannot be treated within currently available transient network theories where all chains are linked to a network. A self-contained systematic theory for the dynamics of these solutions must allow constant exchange between unconfined free chains and chains in a network.

For simplicity, we assume there are two associating groups per chain at its ends. A chain is *effective* when both ends are incorporated in the network, and it is *dangling* when only one end is bonded to a jucntion as shown in Figure 1. The more complicated situation involving more than two functional groups per chain located in positions other than ends is more general, but it should not change the qualitative conclusion of the simplified model. Like TE,[11] we consider only the case where the network is formed by unentangled chains so that its dynamics are completely specified by rates of creation and destruction of junctions. Extension to entangled networks and to chains with more associating groups will be one direction of future works. Since the TE type theory is not capable of explaining shear-thickening phenomena, important modifications are required. In contrast to the TE theory, in our model the dangling chains are allowed to become free with a certain probability and free chains can also become dangling. Therefore there is a proper distribution of effective, dangling, and free chains as schematically shown in Figure 1. A shear flow plays three roles in influencing this distribution: (i) It deforms the temporary network or large clusters affinely. (ii) It changes the rate at which effective chains become dangling and junctions are destroyed. (iii) It increases the number of effective chains by inducing coagulation between free chains and a network. When the last effect of shear is dominant, shear thickening may take place. This may be the case when the concentration falls within a certain range and shear rate $\dot{\gamma}$ takes on intermediate values.

This paper is concerned with steady-state viscosity and normal stress differences as functions of time-independent $\dot{\gamma}$. Up to now few experimental observations of dynamic moduli and transient flow behaviors of shear-thickening systems have not been published; therefore, we will defer calculation of transient and oscillatory rheological properties to a future study. We begin in section II with a derivation of our model that reduces to the TE model in a special case. Steady-state number density distribution of three different types of chains is calculated in section III and steady-state stress is obtained as a function of strain rate. Our results are discussed in the concluding section IV.

II. Model of Network and Free Chains in Coexistence

A. Premises. The model presented in this paper assumes that (a) the relaxation time of the transient network is much longer than that of the free and dangling chains; (b) the network experiences affine deformation; (c) the elastic portion of stress dominates over the viscous stress. These assumptions have the consequence that the network sustains most of the stress and free and dangling chains contribute negligibly. According to assumption b, the dynamics of the end-to-end distance $\mathbf{r}(t)$ of a confined chain in the network obeys the relation

$$\mathbf{r}(t) = \hat{\epsilon}(t,t')\cdot\mathbf{r}(t') \tag{1a}$$

where $\hat{\epsilon}(t,t')$ is the time-dependent deformation gradient tensor, normally denoted by $\hat{F}(t,t')$ in the literature of rheology. If the rate of deformation is independent of time, i.e., the deformation is time-invariant, $\hat{\epsilon}$ can be written as

$$\hat{\epsilon}(t,t') \equiv \hat{\epsilon}(t-t') = e^{\Gamma(t-t')} \tag{1b}$$

where Γ is the velocity gradient tensor. Assumption d of our model states that free and dangling chains are Gaussian and that their motion follows the Langevin dynamics. On a time scale of the network relaxation, the time-averaged end-to-end distance $\bar{\mathbf{R}}$ of these free and partially free chains can be described by a time-independent distribution function $\psi(\bar{\mathbf{R}})$. It will become clear that because of assumption a we can replace $\psi(\bar{\mathbf{R}})$ by the Gaussian distribution, i.e.

$$\psi(R) = \left(\frac{3}{2\pi\langle\mathbf{R}^2\rangle_0}\right)^{3/2}\exp\left(-\frac{3\mathbf{R}^2}{2\langle\mathbf{R}^2\rangle_0}\right) \tag{2}$$

for all practical purposes,[12] where here and below the bar over $\mathbf{R}$ has been and will be omitted. The average squared end-to-end distance is related to the number of segments in a chain by $\langle\mathbf{R}^2\rangle_0 = Nl^2$ where l is the length of a statistical segment.

B. Chain Distribution Functions. Suppose the solution of associating particles is macroscopically homogeneous in both the absence and presence of flow. Denote the total number density in a fluid element by n. It remains constant in time for an incompressible fluid that we consider here. Let us introduce the following notations for the distribution functions of the three types of chains in the solution: $\phi^{\mathrm{E}}[\mathbf{r}(t),t]\,\mathrm{d}\mathbf{r}(t)$ is the number of effective chains per unit volume whose end-to-end distances are within the volume element $(\mathbf{r}(t),\mathbf{r}(t)+\mathrm{d}\mathbf{r}(t))$ at time t assuming the deformation of the form (1b) was applied at $t = 0$. $\phi^{\mathrm{D}}[\mathbf{R},t]\,\mathrm{d}\mathbf{R}$ designates the number of dangling chains per unit volume with their end-to-end vectors between $\mathbf{R}$ and $\mathbf{R} + d\mathbf{R}$. Finally $\phi^F[\mathbf{R},t]\, d\mathbf{R}$ gives the number of free chains per unit volume with their end-to-end vectors between $\mathbf{R}$ and $\mathbf{R} + d\mathbf{R}$. In order to derive equations of motion for ϕ^E, ϕ^D, and ϕ^F, let us divide the continuous time into discrete steps of unit Δt that is small on the experimental time scales but large compared to the relaxation time τ of each ineffective chain. For simplicity it is reasonable to suppose that free chains cannot turn into effective chains in a single time step of Δt and the reverse is also true. At time $t_i = i\Delta t$, the number density $\phi^E(\mathbf{r}_i,t_i)$ of effective chains can be obtained in terms of its value at the earlier time $t_{i-1} = (i-1)\Delta t$ and of the population of dangling chains

$$\phi^E(\mathbf{r}_i,t_i) = [1 - \beta(\mathbf{r}_{i-1})\Delta t]\phi^E(\mathbf{r}_{i-1},t_{i-1}) + p\Delta t\phi^D(\mathbf{r}_i,t_{i-1}) \quad (3)$$

where β is the probability for breakage of effective chains per unit time. The β function may depend on the chains' end-to-end distances $\mathbf{r}_{i-1}$, since tension in the chains, as a function of $\mathbf{r}_{i-1}$, can affect the breakage rate. The parameter p is the probability that a dangling chain joins a junction to become effective in a unit time interval. The first term of (3) represents the number of effective chains remaining that have been effective from $t_0 = 0$ up to t_i. The second term indicates that only dangling chains whose end-to-end vectors at time t_{i-1} happen to be within the range of $(\mathbf{r}_i, \mathbf{r}_i + d\mathbf{r}_i)$ will have the probability of p to have their other ends connected to junctions. These junctions are assumed to be capable of taking more than two chain ends.

Kinetic equations similar to (3) can be obtained for dangling and free chains. Suppose α is the probability per unit time for a dangling chain to disappear. Let μ be the probability that a free chain joins the network to become a dangling chain in a unit time. Depending on conversion processes, μ may be a function of the velocity gradient tensor Γ introduced in (1b). For a simple shear flow, μ may be a strongly increasing function of shear rate $\dot{\gamma}$ due to the Smoluchowski mechanism of shear-induced coagulation. On the other hand, for an extension flow, μ could be a decreasing function of the rate of deformation $\dot{\epsilon}$. The equation for the dangling chain density ϕ^D can be written as

$$\phi^D(\mathbf{R},t_i) = (1 - \alpha\Delta t)\phi^D(\mathbf{R},t_{i-1}) + \mu\Delta t\phi^F(\mathbf{R},t_{i-1}) + \Delta t\psi(\mathbf{R})\, g_{E\to D}(t_{i-1}) \quad (4)$$

where the chain generation function $g_{E\to D}$ is defined by

$$g_{E\to D}(t) \equiv \int d\rho\, \beta(\rho)\phi^E(\rho,t) \quad (5)$$

Here and below the vector ρ is a dummy integration variable. The spatial integration in (5) indicates that $g_{E\to D}$ gives the number of dangling chains generated from effective chains regardless of their end-to-end distance per unit time per unit volume at time t. The first term in (4) means the number of dangling chains has decreased by a fraction of $\alpha\Delta t$ in a period of Δt, the second term says the population of dangling chains increases when the network captures free chains, and the third gives the number of effective chains converted to dangling ones per unit volume in this one time step. In writing down the third term in (4), use is made of the fact that once an end of an effective chain has been released from the network at time t_{i-1} it will take conformations of a free chain described by ψ of (2) after a period of $\Delta t \gg \tau$. Lastly we find the recursion relation for the distribution function of free chains to be given by

$$\phi^F(\mathbf{R},t_i) = (1 - \mu\Delta t)\phi^F(\mathbf{R},t_{i-1}) + q\Delta t\phi^D(\mathbf{R},t_{i-1}) \quad (6)$$

where q is the probability per unit time that a dangling chain detaches itself from the network to become free and it is related to the other two probabilities α and p by $q = \alpha - p$. The first term in (6) has a similar meaning to that in (4), and the second term simply states that the increment in the number of free chains due to release of dangling chains is proportional to their number density ϕ^D.

The difference equations (3), (4), and (6) have established the analytical foundation of our theory, and their solutions can be obtained by converting them to differential equations. Thus we rewrite (4) and (6) in differential form in the limit of $\Delta t \to 0$ as

$$\frac{\partial\phi^D(\mathbf{R},t)}{\partial t} = \mu\phi^F(\mathbf{R},t) + \psi(\mathbf{R})\, g_{E\to D}(t) - \alpha\phi^D(\mathbf{R},t) \quad (7)$$

and

$$\frac{\partial\phi^F(\mathbf{R},t)}{\partial t} = (\alpha - p)\phi^D(\mathbf{R},t) - \mu\phi^F(\mathbf{R},t) \quad (8)$$

where the function $\psi(\mathbf{R})$ is the Gaussian distribution given in (2). It is straightforward to integrate these two first-order differential equations to provide the following expressions for the dangling chain distribution

$$\phi^D(\mathbf{R},t) = e^{-\alpha t}\phi^D(\mathbf{R},0) + \int_0^t dt'\, e^{-\alpha(t-t')}[\psi(\mathbf{R})\, g_{E\to D}(t') + \mu\phi^F(\mathbf{R},t')] \quad (9)$$

and for the free chain distribution

$$\phi^F(\mathbf{R},t) = e^{-\mu t}\phi^F(\mathbf{R},0) + (\alpha - p)\int_0^t dt'\, e^{-\mu(t-t')}\phi^D(\mathbf{R},t') \quad (10)$$

where the first term in each of (9) and (10) vanishes in the limit of long times ($t \to \infty$), implying that the initial conditions will be forgotten through the dynamic exchange between the three types of chains. The chain generation function $g_{E\to D}$ appearing in (9) has been given in (5). Clearly the two solutions are in the form of integral equations and are not independent of each other. Moreover, (9) and (10) are incomplete without the input of ϕ^E through (5).

The difference equation (3) for the network dynamics can also be transformed to a differential equation. Since the two vectors $\mathbf{r}_i$ and $\mathbf{r}_{i-1}$ are related to each other according to (1b) as $\mathbf{r}_i = e^{\Gamma\Delta t}\cdot\mathbf{r}_{i-1}$, a Taylor expansion to first order in Δt yields $\mathbf{r}_i - \mathbf{r}_{i-1} = \Delta t\Gamma\cdot\mathbf{r}_{i-1} \equiv \Delta t\mathbf{v}(\mathbf{r}_{i-1})$. Passing to the continuum limit with $i\Delta t \to t$, (3) becomes in the limit of $\Delta t \to 0$

$$\frac{\partial\phi^E(\mathbf{r},t)}{\partial t} + \mathbf{v}(\mathbf{r})\cdot\nabla\phi^E(\mathbf{r},t) = p\phi^D(\mathbf{r},t) - \beta(\mathbf{r})\,\phi^E(\mathbf{r},t) \quad (11)$$

with the velocity field defined by

$$\mathbf{v}(\mathbf{r}) = \Gamma\cdot\mathbf{r} \quad (12)$$

where Γ is the velocity gradient tensor defined in (1b). The first-order partial differential equation can be integrated using the method of characteristics as Fuller and Leal[13] did for the Yamamoto equation. For practical calculations, an integral equation for ϕ^E is more useful. To this end, we iterate the recursive equation (3) and replace the resulting discrete sums by integrals by taking $\Delta t \to$

0 to find

$$\phi^{E}(\mathbf{r},t)\,\mathrm{d}\mathbf{r} = \exp\{-\int_0^t \mathrm{d}t'\, \beta[\hat{\epsilon}(t')\cdot\rho]\}\phi^{E}(\rho,0)\,\mathrm{d}\rho + p\int_0^t \mathrm{d}t' \exp\{-\int_{t'}^{t} \mathrm{d}t''\, \beta[\hat{\epsilon}(t''-t')\cdot\mathbf{r}']\}\phi^{D}(\mathbf{r}',t')\,\mathrm{d}\mathbf{r}' \quad (13)$$

where the argument of the β function has been explicitly displayed using (1a) and (1b). When we substitute (10) into (9), the resulting equation together with (13) amounts to a set of *coupled* integral equations for ϕ^{E} and ϕ^{D}. Expressions (9), (10), and (13) are the central results of this section. When the probabilities α and p satisfy $\alpha = p$, dangling chains can no longer become free. In this case, no free chains exist at long times according to (10) and the equation (13) reproduces the recent transient network theory of Tanaka and Edwards.[11]

III. Dynamic Balance of Chain Exchange and Stress Tensor

A. Chain Number Densities and Exchange Rates. In this subsection we are interested in the stationary populations of each type of chains and the steady-state exchange rates between these chains. The number densities $n_E(t)$, $n_D(t)$, and $n_F(t)$ at a given time are simply spatial integrations of the chain distribution functions of (9), (10), and (13), respectively. We recall assumption d in subsection II.A and accordingly conclude that the distribution functions for the ineffective chains always have the form

$$\phi^{D,F}(\mathbf{R},t) \equiv n_{D,F}(t)\,\psi(\mathbf{R}) \quad (14)$$

where the super- and subscript "D,F" indicate that the expression holds for both free and dangling chains, and $\psi(\mathbf{R})$ is given by (2). Substituting (14) into (7), (8), and (11), the resulting equations, after integration over space, become rate equations of the form familiar in chemical reactions. The solutions of these rate equations can be directly derived from (9), (10), and (13) together with (14) after spatial integration

$$n_D(t) = n_D(0)\, e^{-\alpha t} + \int_0^t \mathrm{d}\lambda\, e^{-\alpha\lambda}[g_{E\rightarrow D}(t-\lambda) + \mu n_F(t-\lambda)] \quad (15)$$

$$n_F(t) = n_F(0)\, e^{-\mu t} + (\alpha - p)\int_0^t \mathrm{d}\lambda\, e^{-\mu\lambda} n_D(t-\lambda) \quad (16)$$

and

$$n_E(t) = n_E^{\mathrm{int}}(t) + p\int_0^t \mathrm{d}\lambda\, \theta(\Gamma,\lambda)\, n_D(t-\lambda) \quad (17)$$

where a change has been of the integration variable $\lambda = t - t'$. In (17) n_E^{int} is the number of effective chains per unit volume that initially formed the network and still remain effective until the present time t and is given by

$$n_E^{\mathrm{int}}(t) = \int \mathrm{d}\rho\, \phi^{E}(\rho,0) \exp\{-\int_0^t \mathrm{d}t'\, \beta[\hat{\epsilon}(t')\cdot\rho]\} \quad (18)$$

Like the first terms in (15) and (16), $n_E^{\mathrm{int}}(t)$ also vanishes as $t \rightarrow \infty$. The propagator θ has a form similar to (18) and is defined by

$$\theta(\Gamma,\lambda) = \int \mathrm{d}\rho\, \psi(\rho) \exp\{-\int_0^\lambda \mathrm{d}t'\, \beta[\hat{\epsilon}(t')\cdot\rho]\} \quad (19)$$

where the velocity gradient tensor Γ is related to the deformation gradient tensor $\hat{\epsilon}(t)$ by (1b) and the functional form of β has not been specified yet. Equations 15, 16, and 17 are coupled linear inhomogeneous integral equations for the chain number densities. These seemingly complicated integral equations can be turned into simple algebraic equations by applying the method of Laplace transformation: $\tilde{n}_A(s) = \mathcal{L}n_A(t)$ where the subscript A stands for either E, D, or F. The solution $n_A(t)$ in real time t can be calculated in terms of residues of the function $\tilde{n}_A(s)\, e^{st}$. In this paper we focus on steady-state features at long times.

In the long time limit, results are particularly simple. For example, it is obvious from (19) that $\theta(\Gamma,\lambda)$ becomes exponentially small when the time variable $\lambda > 1/\beta_{\min}$ where $\beta_{\min} = \min\{\beta(\mathbf{r}), \mathbf{r} \in \text{full space}\}$. Thus at times $t \gg \lambda \approx 1/\beta_{\min}$, (17) can be rewritten as

$$\nu(\Gamma)\, n_E^* = p n_D^* \quad (20)$$

where the function $\nu(\Gamma)$ has the physical meaning of a probability in unit time for effective chains to be converted to dangling chains and is defined by the integral

$$\frac{1}{\nu(\Gamma)} = \int_0^\infty \mathrm{d}\lambda\, \theta(\Gamma,\lambda) \quad (21)$$

and the asterisk indicates stationary quantities. Similarly we replace (16) by

$$\mu(\Gamma)\, n_F^* = (\alpha - p) n_D^* \quad (22)$$

in the long time limit of $t\beta_{\min} \gg 1$, where the probability μ is explicitly written as an unspecified function of Γ. It is not necessary to rewrite (15) because use can be made of the conservation law: $n = n_E^* + n_D^* + n_F^*$. Finally we find

$$n_D^* = \frac{n}{1 + p/\nu(\Gamma) + (\alpha - p)/\mu(\Gamma)} \quad (23a)$$

$$n_F^* = \left[\frac{(\alpha - p)}{\mu(\Gamma)}\right] n_D^* \quad (23b)$$

and

$$n_E^* = \left[\frac{p}{\nu(\Gamma)}\right] n_D^* \quad (23c)$$

where $\nu(\Gamma)$ is given by (21) and $\mu(\Gamma)$ remains to be specified. We expect the phenomenological parameter p to be a sharp function of concentration n so that the number of network-forming effective chains abruptly increases from zero to a finite value at a critical percolation point n_c.[14] For concentrations $n < n_c$ where $p \approx 0$, viscoelastic properties of the solution depend on those of free and dangling chains and can be described by a dynamic theory, e.g., for polyelectrolyte solutions. But the present study does not address this topic. The number of effective chains can also be made large by taking a large ratio of $p/\nu(\Gamma)$. This would correspond to the limit of strong gelation. In the limit where dangling chains are few compared to effective and free ones, unity in the denominator of (23b), where the other terms are much larger than 1, drops out. In this situation, there is almost a direct exchange between effective and free chains and dangling is a state in which chains would expend little time. Similarly the number of free chains can be chosen to be small by setting $\alpha \approx p$. Thus by allowing a range of values for the magnitude of these phenomenological parameters, our model can deal with a whole variety of experimental systems and thermodynamic conditions. In this context, we have implicitly taken the probabilities α, β, p, and μ to be, in principle, functions of concentration and other thermodynamic variables. Looking back at the relations (20) and (22), we see that they represent the steady-state balance for exchange between the three different kinds of chains. Thus in a unit time, the number of chains exchanged between effective and dangling chains in a unit volume is

$$w(\mathrm{E}\leftrightarrow\mathrm{D}) = n\left[\frac{p}{1 + p/\nu(\Gamma) + (\alpha - p)/\mu(\Gamma)}\right] \quad (24a)$$

and similarly we have

$$w(\mathrm{F}\leftrightarrow\mathrm{D}) = n\left[\frac{\alpha - p}{1 + p/\nu(\Gamma) + (\alpha - p)/\mu(\Gamma)}\right] \quad (24b)$$

The two-way arrows in (24a) and (24b) clearly show our assumption of *stepwise* exchange; namely, there is no direct conversion between effective and free chains. The exchange rates w are proportional to the total chain number density n as expected. Setting $\Gamma = 0$ in (23a)–(23c) and in (24a) and (24b) produces the equilibrium results.

B. Calculation of the Stress Tensor. We assume that the elastic energy of effective chains dominates and can be expressed in the form of a harmonic spring. Application of deformation to the system will affinely stretch these chains in the transient network on a time scale of the inverse of $\nu(\Gamma)$ defined in (21). On this time scale where $\nu^{-1}(\Gamma) \gg \tau$, free and dangling chains have already relaxed to their stress-free state unless the strain rate $|\Gamma|$ exceeds τ^{-1}. When the condition $|\Gamma| \approx \tau^{-1} \gg \nu(\Gamma)$ is true, the deformation in effective chains is so large that nonlinear effects arise to invalidate the harmonic form of the elastic energy. We only consider $|\Gamma|$ not too large compared to $\nu(\Gamma)$. Under this circumstance free and dangling chains are simply in their equilibrium conformations described by the Gaussian distribution of (2). Thus only resistance from *effective* chains generates stress in the system. For a harmonic chain of average squared end-to-end distance $\langle \mathbf{R}^2\rangle_0 = Nl^2$, its Hookian constant is given by $K = 3k_BT/Nl^2$. The stress tensor due to effective chains has the standard form

$$\sigma(t) = K\langle \mathbf{r}(t)\,\mathbf{r}(t)\rangle_{\phi^\mathrm{E}} \quad (25)$$

where the subscript ϕ^E of the angular brackets denotes integration of the diadic product $\mathbf{rr}$ over the distribution function ϕ^E of (13). In the steady state, i.e., at long times, the calculation of stress tensor σ is greatly simplified to

$$\sigma^*(\Gamma) = K\mathrm{n_E}^*\nu(\Gamma)\int_0^\infty \mathrm{d}\lambda \int \mathrm{d}\rho[\hat{\epsilon}(\lambda)\cdot\rho\hat{\epsilon}(\lambda)\cdot\rho] \times \psi(\rho)\exp\{-\int_0^\lambda \mathrm{d}t'\,\beta[\hat{\epsilon}(t')\cdot\rho]\} \quad (26)$$

where the time-dependent deformation gradient tensor $\hat{\epsilon}(t)$ is defined by (1b), the number density $\mathrm{n_E}^*$ of effective chains in the network is given by (23c), and $\psi(\rho)$ is the end-to-end vector distribution of (2). The mathematical statement of affine deformation (1a,b) has been introduced in the transition from (25) to (26). Expression (26) for stress due to networking is the key formula of this paper. Once the analytical form of the velocity gradient tensor Γ is specified and an explicit expression of the β function is given, elementary computations can be performed to evaluate the steady-state stress tensor $\sigma^*(\Gamma)$ as a function of Γ.

For a simple shear flow of shear rate $\dot{\gamma}$, Γ is an asymmetric tensor with only one nonzero component given by

$$\Gamma = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (27)$$

for which the deformation gradient tensor reads, according to (1b)

$$\hat{\epsilon}(t) = \begin{pmatrix} 1 & \dot{\gamma}t & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (28)$$

Under the assumption of affine deformation (1a,b), the degree of stretching of effective chains is proportional to the strain $\dot{\gamma}t$. Because an effective chain could only survive for a period of $1/\nu(\Gamma) \approx 1/|\beta|$, the affine deformation to the chain is not severe for $\dot{\gamma}/|\beta| \leq 1$, where $|\beta|$ just indicates the magnitude of the breakage rate β. Therefore, when the shear rate $\dot{\gamma}$ is not large compared to the relaxation rate of the network, tension in an effective chain is not significantly greater than that under the quiescent condition and β can be taken as a constant independent of the end-to-end distance. For a strong shear with $\dot{\gamma}/|\beta| \gg 1$, the chain tension due to large deformation *may* cause effective chains to break off from junctions more frequently than in absence of flow, leading to an increasing function for β. One convenient and physically sensible form for β is

$$\beta[\mathbf{r}(t)] = \beta_0\left(1 + \delta\frac{|\mathbf{r}(t)|^2}{Nl^2}\right) \quad (29)$$

where β_0 provides a measure of the order of magnitude of β and δ is an important phenomenological parameter in our model. If junctions in the transient network are very strong, then the chain tension cannot drastically alter the breakage rate and therefore β will be a very weak function of $\mathbf{r}$. This can be realized by choosing $\delta \ll 1$. On the other hand, for networks with weak junctions we can take δ close to unity.

B.1. Strong Network Limit. We consider a transient network formed with strong junctions,[15] take the parameter $\delta = 0$, and derive the shear viscosity η and first normal stress difference N_1 in closed analytical form. Inserting (29) for β into (26) and carrying out one Gaussian integration and another integration involving an exponential function, we find the following results for η:

$$\eta(\dot{\gamma}) = \sigma_{xy}(\dot{\gamma})/\dot{\gamma} = G(\dot{\gamma})\,\tau_\mathrm{network} \quad (30)$$

where the asterisk in (26) is omitted here and below and the relaxation time τ_network of the network is calculated by substituting (29) into (21) and using (19).

$$\tau_\mathrm{network} = \frac{1}{\nu(\dot{\gamma})} = \frac{1}{\beta_0} \quad (31)$$

The modulus G of the dynamic network is proportional to the number density $\mathrm{n^{E*}}(\dot{\gamma})$ of effective chains

$$G(\dot{\gamma}) = \mathrm{n_E}^*(\dot{\gamma})\,k_BT = \left[\frac{(p/\beta_0)}{1 + p/\beta_0 + (\alpha - p)/\mu(\dot{\gamma})}\right]nk_BT \quad (32)$$

The general structure of (30) is standard in viscoelastic theories for polymer solutions, and that of (32) involving the first equality is a basic expression in classical rubber elasticity theories. The normal stress N_1 can be evaluated in a similar fashion from (26) as

$$N_1 = \sigma_{xx} - \sigma_{yy} \equiv \Psi_1(\dot{\gamma})\,\dot{\gamma}^2 = 2G(\dot{\gamma})\,(\dot{\gamma}\tau_\mathrm{network})^2 \quad (33)$$

where Ψ_1 is called the first normal stress coefficient. It is also interesting to note that the formula (33) for N_1, given in terms of the modulus G and relaxation time τ_network, has the same form as that of the preaveraged Rouse–Zimm (RZ) bead–spring model. Like RZ's preaveraged theory, the second normal stress difference defined by $N_2 = \sigma_{yy} - \sigma_{zz}$ is found to be zero in this case of strong networks.

Since the network relaxation time τ_{network} is independent of the shear rate $\dot\gamma$ for a constant β, the $\dot\gamma$-dependence of the shear velocity η comes solely from that of the number density $n_E^*(\dot\gamma)$. The number of effective chains n_E^* increases with $\dot\gamma$ as more free chains collide into and join the existing network with aid of the simple shear flow. This causes an increase in viscosity according to (30) and (32). The shear-thickening behavior is characterized by the shear-rate-dependent probability $\mu(\dot\gamma)$ of converting free chains to dangling chains per unit time. One simple analytical form for μ is $\mu(\dot\gamma) = \mu_0 + \mu_1\dot\gamma^2$ where μ_0 originates from Brownian motion of chains and the constant μ_1 has the dimension of time. More generally, any montonously increasing function for $\mu(\dot\gamma)$ will produce a monotonously increasing function for G in (32). Thus both shear viscosity $\eta(\dot\gamma)$ and the first normal stress coefficient $\Psi_1(\dot\gamma)$ increase with shear rate $\dot\gamma$. So for systems to which the present calculation applies, shear thickening will be accompanied by an increasing function of $\Psi_1(\dot\gamma)$. To our knowledge measurement of Ψ_1 has not been performed for shear-thickening fluids. Usually the shear thickening is taken over by shear thinning at higher $\dot\gamma$. The special consideration given in this minisection predicts no such subsequent shear thinning. Consequently we need to go back to the general form of (29) and to introduce it into the formula (26) for the steady-state stress tensor.

It is difficult to visualize a situation where the conversion probability p (from dangling to effective) would become a function of strain rate Γ, unless Γ is as high as τ^{-1}. Even if p is strain-rate-dependent, it is not easy to argue for an *increasing* function of $p(\Gamma)$, which would produce shear thickening in (30) and (32) without the presence of free chains, i.e., for $\alpha = p$. Within the context of the Lodge network model, such a relationship between the chain creation process and strain rate has previously been introduced to characterize rheological properties of polymer melts.[16] From our point of view, shear thickening is unlikely if a self-associating system does not possess free chains in dynamic exchange with the network-forming chains.

B.2. General Case. The evaluation of (26) with the β function (29) requires several integrations. Substituting (2) for ψ and (29) for β into (26), we find shear stress and normal stresses to be given, in terms of a three-dimensional Gaussian integral followed by a second integral involving an exponential function

$$\left.\begin{matrix}\sigma_{xy}(\dot\gamma)\\ \sigma_{xx}(\dot\gamma)\\ \sigma_{yy}(\dot\gamma)\\ \sigma_{zz}(\dot\gamma)\end{matrix}\right\} = Kn_E^*\nu(\dot\gamma)\int_0^\infty d\lambda\int_{-\infty}^\infty dx\int_{-\infty}^\infty dy\int_{-\infty}^\infty dz\left(\frac{3}{2\pi Nl^2}\right)^{3/2} \begin{bmatrix}(x+\dot\gamma\lambda y)y\\ (x+\dot\gamma\lambda y)^2\\ y^2\\ z^2\end{bmatrix}\exp\left(-\frac{3(x^2+y^2+z^2)}{2Nl^2}\right)\times \exp\left[-\beta_0\int_0^\lambda dt'\left(1+\delta\frac{(x+\dot\gamma t'y)^2+y^2+z^2}{Nl^2}\right)\right] \quad (34)$$

where integration in the argument of the second exponential function is elementary and the resulting three-dimensional integral containing a Gaussian distribution can be readily evaluated as well. Thus we finally obtain shear viscosity expressed in terms of a single integration that can be readily integrated numerically

$$\eta(\dot\gamma) = \sigma_{xy}(\dot\gamma)/\dot\gamma = G(\dot\gamma)\tau_{\text{network}}(\dot\gamma) \quad (35a)$$

where the relaxation time of the network is defined by

$$\beta_0\tau_{\text{network}}(\dot\gamma) = \frac{f(\bar{\dot\gamma})}{g(\bar{\dot\gamma})},\ \bar{\dot\gamma} \equiv \dot\gamma/\beta_0 \quad (35b)$$

with the dimensionless functions f and g defined by the following one-dimensional integrals

$$f(\bar{\dot\gamma}) \equiv \int_0^\infty dt\, e^{-t}t(1+\delta t/3)(1+2\delta t/3)^{-1/2}[(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9]^{-3/2} \quad (35c)$$

and

$$g(\bar{\dot\gamma}) \equiv \frac{\beta_0}{\nu(\bar{\dot\gamma})} \equiv \int_0^\infty dt\, e^{-t}(1+2\delta t/3)^{-1/2}[(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9]^{-1/2} \quad (35d)$$

where δ is the parameter introduced in (29). Like (31), (35b) indicates that the relaxation time of the network is on the order of $1/\beta_0$ unless $\bar{\dot\gamma} \gg 1$. We know from viscoelastic theories for nonassociating polymer solutions that the contribution of dangling and free chains to solution viscosity η is of the magnitude $(n_D^* + n_F^*)k_BT\tau$ where τ is the relaxation time of an unrestricted chain. Since we have $\tau_{\text{network}} \approx 1/\beta_0 \gg \tau$, this correction is indeed small. The network modulus G in (35a) is given by

$$G(\dot\gamma) = n_E^*(\dot\gamma)\,k_BT = \left[\frac{(p/\beta_0)g(\bar{\dot\gamma})}{1+(p/\beta_0)g(\bar{\dot\gamma})+(\alpha-p)/\mu(\dot\gamma)}\right]nk_BT \quad (35e)$$

where the function g has been defined in (35d). In contrast to (31) for strong networks, now relaxation time τ_{network} of the network depends on the shear rate and as expected it decreases with increasing $\dot\gamma$ according to (35b), (35c), and (35d). But the dependence is very weak when $\bar{\dot\gamma} < 1$.

Similarly the normal stresses are obtained by substituting (29) into (26) and by performing similar integrations as done for the shear stress of (35a)

$$\sigma_{ii}(\dot\gamma) = G(\dot\gamma)\, g(\bar{\dot\gamma})\, h_{ii}(\bar{\dot\gamma}^2) \quad (36a)$$

where the subscript ii denotes either xx or yy or zz and the functions h_{ii} are defined as

$$h_{xx}(\bar{\dot\gamma}^2) \equiv \int_0^\infty dt\, e^{-t}(1+2\delta t/3)^{-3/2}[(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9]^{-1/2}\left\{1 + \bar{\dot\gamma}^2t^2\left[\frac{(1+2\delta t/3)^2 - 2(1+2\delta t/3)\delta t/3 + \delta^2t^2/9}{(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9}\right]\right\} \quad (36b)$$

$$h_{yy}(\bar{\dot\gamma}^2) \equiv \int_0^\infty dt\, e^{-t}(1+2\delta t/3)^{1/2}[(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9]^{-3/2} \quad (36c)$$

and

$$h_{zz}(\bar{\dot\gamma}^2) \equiv \int_0^\infty dt\, e^{-t}(1+2\delta t/3)^{-3/2}[(1+2\delta t/3)^2 + \bar{\dot\gamma}^2t^2(2\delta t+\delta^2t^2/3)/9]^{-1/2} \quad (36d)$$

For a finite δ, we find that the second normal stress difference is no longer zero and it possesses an *opposite* sign to that of the first normal stress difference. Ordinary polymer solutions often have opposite signs for their first and second normal stress differences as well. Because the function $f(\dot{\bar{\gamma}})$ of (35c) decreases with reduced shear rate $\bar{\gamma}$, shear thickening may occur in the range of shear rates $\dot{\gamma} \leq 1/\beta_0$ where $\mu(\dot{\gamma})$ increases with $\dot{\gamma}$ while $f(\dot{\bar{\gamma}})$ is still nearly a constant. At high shear rates, i.e., for $\dot{\bar{\gamma}} \gg 1$, the behavior of $f(\dot{\bar{\gamma}})$ dominates in (35a)–(35e) and the system becomes shear-thinning. This can be demonstrated for several sets of parameters δ, p, α, and the quadratic function $\mu(\dot{\gamma})$ with specified constants μ_0 and μ_1. We calculate the shear viscosity $\eta(\dot{\gamma})$ of (35a) by numerically evaluating the integrals (35c) and (35d) as a function of the reduced shear rate $\dot{\bar{\gamma}}$. For convenience, take $p = \beta_0$ and denote $\bar{q} = (\alpha - p)/\mu_0$ and $r = \mu_1\beta_0^2/\mu_0$ in (35e) so that (35a) can be rewritten in the following explicit form:

$$\bar{\eta}(\dot{\bar{\gamma}}) = \frac{\eta(\dot{\bar{\gamma}})}{\eta_0} = \frac{f(\dot{\bar{\gamma}},\delta)(1 + r\dot{\bar{\gamma}}^2)[\bar{q} + 1 + g(0,\delta)]}{f(0,\delta)\{\bar{q} + [1 + g(\dot{\bar{\gamma}},\delta)](1 + r\dot{\bar{\gamma}}^2)\}} \tag{37}$$

where η_0 is the viscosity at a vanishing shear rate and δ-dependence of functions f and g of (35c) and (35d) is explicitly indicated. Three groups of the adjustable phenomenological parameters δ, $\bar{q}$, and r are chosen. In Figure 2a we compare the set $\delta = 0.2$, $\bar{q} = 10$, and $r = 10$ with that of $\delta = 0.2$, $\bar{q} = 20$, and $r = 10$. It is clearly seen that the larger $\bar{q}$ gives rise to a stronger shear thickening. Since $\bar{q}$ is proportional to the initial free chain density, this result is consistent with the physical picture described by the model. Next we see that the role of r is to determine the critical shear rate for shear thickening, as shown in Figure 2b: the larger r is, the smaller the shear rates at which shear thickening takes place. Again this is reasonable because r measures how effectively the shear flow is able to convert free chains to dangling ones. The eventual shear thinning after shear thickening will be delayed if the network breakage rate cannot be not strongly reduced by the shear flow. This is controlled by the parameter δ introduced in (29). In Figure 2c results for different values of δ are presented.

IV. Discussion and Conclusion

We have extended previous transient network models to allow for the coexistence of network-forming chains and unconfined free chains. The present model for reversible network systems with temporary cross-links, being the first of its kind, suggests the presence of three types of chains under certain circumstances: stress-bearing *effective* chains, dangling chains with one end attached to the network, and individual chains free of interchain bonding. It has been assumed that free chains must go through the dangling state before they become effective, and kinetic exchanges between free and dangling chains and between dangling and effective chains lead the system to its equilibrium or steady state. By the notion of network formation, we have taken the relaxation time of a network to be much longer than that of a free or dangling chain. This consideration has permitted us to calculate stress due to affine deformation of network structures. To avoid complications arising from entanglement, we only treated the unentangled situation where formation of a network is due solely to junctions among functional groups at chain ends. Coagulation of free chains into networks, enhanced by shear flow, produces more effective chains in steady shear than in equilibrium. Our model, when taking the shear-induced coagulation into account, explains shear thickening as due to more chains participating in networking. At high shear rates $\dot{\gamma}$, where the rate β for chain breakage increases with $\dot{\gamma}$ and the relaxation time of the network shortens, junctions break up frequently and the system starts to show shear thinning.

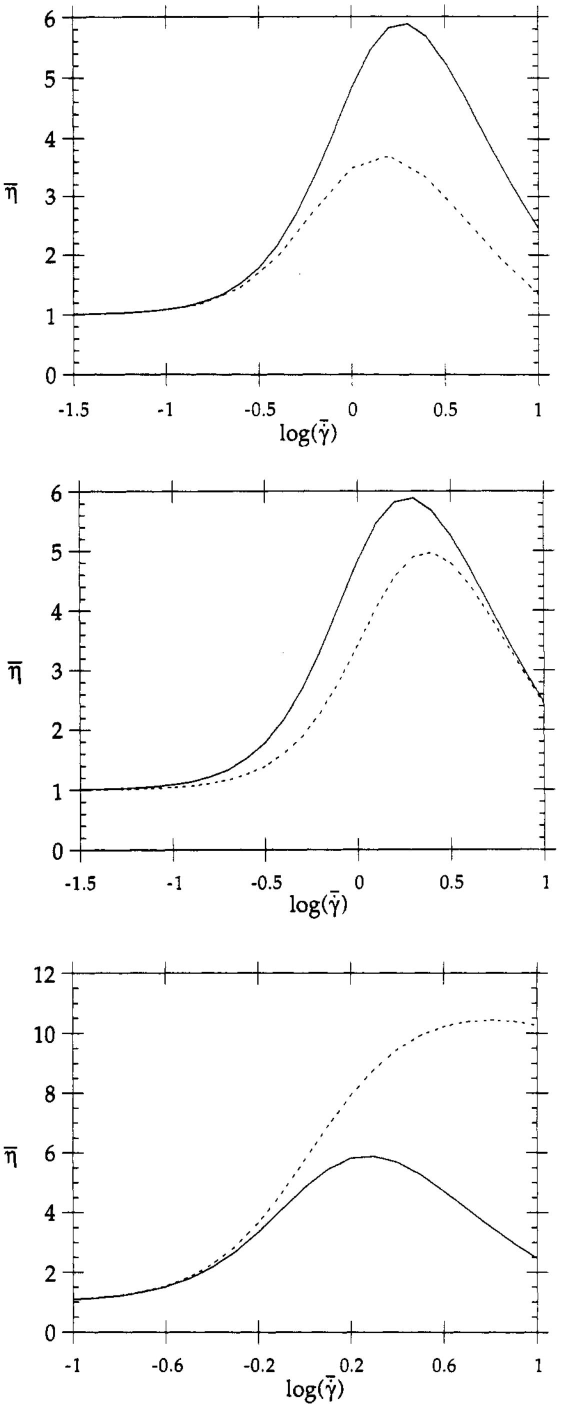

Figure 2. Shear viscosity as a function of dimensionless shear rate. The solid curves have the same set of parameters: $\delta = 0.2$, $\bar{q} = 20$, $\bar{r} = 10$. (a) The dashed curve corresponds to $\delta = 0.2$, $\bar{q} = 10$, and $r = 10$. (b) The dashed curve is given by $\delta = 0.2$, $\bar{q} = 20$, and $r = 5$. (c) The dashed curve represents $\delta = 0.0001$, $\bar{q} = 20$, and $r = 10$.

Another possible process leading to shear thickening has been suggested recently by Witten,[6] who proposed that flow should produce more open conformations for the individual chains and therefore should promote interchain pairing by converting intrachain to interchain pairing. However, when the lifetime of pairing is much longer than the relaxation time τ of free chains, as implied in ref 6, flow cannot break *strong* intrachain pairing until most interchain pairings are broken. It is not clear how such a mechanism could give rise to shear thickening.

Under any circumstances, in a shear-thickening system there may be a considerable amount of free chains that become incorporated into networks by shear flow. Unbound chains should also be present in other physically cross-linked systems in an appropriate range of concentration. Therefore, our proposed model should provide a basic framework for dynamic theories of network-forming, reversibly cross-linked systems. Throughout the paper the concept "network" has assumed the physical meaning that it is a structure comprised of chains and junctions with a finite lifetime and it deforms affinely in a flow field. The networks do not have to be infinite or percolative, i.e., as large as the dimensions of the experimental sample.

There are two major directions along which the present model should be extended. One task is to deal with chain entanglement and to allow more functional groups in each chain. In the present theory each strand between adjacent junctions is an effective chain and conservation of the number of chains places a convenient relationship between the number of effective chains and the total chain concentration. More than two associating points in each chain will complicate calculation of the contribution from different chains to the stress tensor. A chain can be elastically active and contributes to sustaining stress even though a portion of it is dangling from the network. Incorporation of entanglements means that there will be more than one kind of junctions that either arise from functional association or are due to entanglement, with different lifetimes. The entanglement points, although being weaker cross-linkers, help form a network that would experience affine deformation and breakup of intrachain ionic (or functional) junctions in flow and convert intrachain associations to interchain junctions, giving rise to a higher viscosity. The second important extension is to include the cases where hydrodynamic viscous stress is a significant part of the total stress. A number of important systems require such an investigation. Rodlike micellar solutions are one example, dispersions of solid particles at high volume fraction are another, and networks synthesized from liquid crystalline polymers are a third.[17]

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(15) Junctions are strong only in the sense that their breakage is insensitive to the conformation of effective chains. Therefore, the limit examined here is different from the strong association assumption of Witten[6] where no dangling chains were allowed and unbound chains exist as "ring" chains with two ends paired to form a ring polymer.

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