Macromolecules **1991,** *24,* 3163–3177

Semiempirical Theory of Relaxation: Concentrated Polymer Solution Dynamics

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Received June 26, 1990; Revised Manuscript Received November 16, 1990

ABSTRACT: Classical models of viscoelasticity neglect memory effects arising from material inhomogeneity and cooperative molecular motion. These memory effects are modeled by using an integral equation approach in which physical arguments are employed to estimate the memory kernel. Our model memory kernel depends on two parameters: β, which is interpreted as a measure of material inhomogeneity, and ϕ, which is interpreted as a measure of cooperativity of molecular motion. Here we apply our relaxation model to polymer melt dynamics. An idealized "cluster" model of stress relaxation in glasses is introduced to estimate β. This model rationalizes well the observed stress relaxation of polymer glasses. A cluster model is also introduced to estimate the molecular weight dependence of the zero-shear rate viscosity and the diffusion coefficient of entangled polymers. For flexible polymers in three dimensions the viscosity molecular weight exponent ranges in the interval 3.3 to 3.7, depending on the strength of the excluded-volume interaction. The diffusion coefficient molecular weight exponent in three dimensions is predicted to lie in the interval −2.3 to −2.5. Results similar to the reptation model are obtained in four dimensions, and the Rouse theory is recovered in the limit of infinite dimensionality. Estimates of the concentration dependence of entangled polymer solution transport properties are also given.

1. Introduction

Some of the most dramatic examples of nonclassical viscoelastic response are observed in concentrated polymer solutions, which are also among the most extensively studied viscoelastic materials.[1] The current theoretical description of concentrated polymer solutions is dominated by the entanglement network model of Bueche[2] and the more recent reptation model of de Gennes[3] and Doi and Edwards.[4] Although these models capture salient aspects of the properties of concentrated polymer solutions, the agreement between theory and experiment is not quantitative. In the Bueche model[2] a realistic estimate of the zero-shear viscosity η_0 dependence on molecular weight ($\eta_0 \sim M^{3.5}$) is obtained, but the molecular weight dependence of the diffusion coefficient D is predicted unrealistically[2,3] ($D \sim M^{-3.5}$). The reptation model[3,4] provides a reasonable estimate of the molecular weight dependence of the diffusion coefficient ($D \sim M^{-2}$), but the molecular weight dependence of the viscosity seems to be inaccurate[1] ($\eta_0 \sim M^3$). Beyond these questions of the numerology of the molecular weight dependence of transport properties a more general theory is needed, which addresses the temperature and concentration dependence of D and η_0, as well as the molecular weight dependence. Furthermore, a description of the time dependence of the stress relaxation is needed, which covers the transition from "glasslike" to "rubberlike" response as well as the transition from the "plateau" to the "terminal zone" (see Ferry[1]).

A full theoretical description of polymer melt dynamics is undoubtedly a challenging task. The first step requires a description of the glass transition in polymers. The Flory–Huggins lattice model provides a starting point for estimating the dependence of the glass transition temperature on chain molecular parameters,[5] but an understanding of the time dependence of stress relaxation in glasses is needed to define an elementary time scale for local molecular motion, the glassy relaxation time, τ_g^*. All transport properties are functions of the time scale τ_g^* (usually discussed[1] in terms of "monomeric friction"), which in turn depends on molecular weight, concentration, pressure, etc., because the glass transition temperature depends on these parameters.[1] For long chains τ_g^* becomes insensitive to chain length so that we can put off an understanding of the glassy dynamics if we confine ourselves to long polymers at constant temperature and pressure. In the second step toward a theoretical description of concentrated polymer solution dynamics, we have to decide what physics is actually responsible for "entanglement" and we have to model this physics to deduce the form of the stress relaxation function describing polymer flow and the dependence of the flow relaxation time, τ_F (the terminal time), on concentration and molecular parameters. Here we attempt a general description of polymer melt dynamics by combining an integral equation approach to relaxation with physical arguments for the polymer melt structure.

In section 2 we summarize a general model of condensed matter relaxation.[6] We start with a formally exact integral equation determining the relaxation of a Hamiltonian dynamical system, which is initially in equilibrium.[7] We argue that material inhomogeneity can lead to a distribution of relaxation times that can break the *apparent* time-translation symmetry of the memory kernel, and a model integral equation is introduced to describe relaxation in inhomogeneous materials. Probablistic arguments, based on Feller's theory of recurrent events,[8–11] are used to further specify a model form of the memory kernel. Exact solutions of the model relaxation function integral equation are summarized and briefly compared with standard empirical relaxation functions for condensed materials. The relaxation function obtained from our model integral equation depends on two parameters ϕ and β, which describe how relaxation is altered from exponential relaxation. The parameter β is interpreted as a measure of material inhomogeneity, and ϕ is interpreted as a measure of the cooperativity of molecular motion.[6]

The integral equation approach to relaxation is applied to polymer melt dynamics in section 3. We construct a memory kernel based on a general conceptual model of viscoelastic materials due to Maxwell[12] and Gemant.[13] In this model the short time relaxation of a viscoelastic material corresponds to a transient elastic response while fluid flow follows as a distinct process at later times.

A specific model of glass structure is needed to specify memory kernel parameters describing glassy stress relaxation. Rivier[14] (see also Vlasov[15] and Nelson et al.[16]) introduced a theory in which a disordered material is considered as a continuum containing defect lines. Accepting this type of defect line model of a glass, we suppose that the energy of a defect line increases in proportion to its length and assume that Boltzmann's law governs the length distribution. From this idealized picture of glassy relaxation we derive a reasonable estimate of the stress relaxation function [a stretched exponential $\exp(-t^{1/3})$ at T_g] and deduce a glassy relaxation time having the Vogel[1,17] form as a leading approximation.

Parallel arguments to the glassy relaxation case are applied to the description of flow in concentrated polymer solutions. We model a concentrated solution of high molecular weight polymers by an ensemble of "amoeba-shaped" entangled chain regions, which rearrange in response to a sustained stress. We argue that the energy of these "clusters" scales with volume and that the volume distribution is governed by Boltzmann's law. A criterion is given for the existence of this entanglement clustering in terms of chain molecular parameters. The relaxation function is obtained as an average over the cluster volume distribution, and a stretched exponential relaxation function ($\exp(-t^{3/5})$) is obtained where the exponent again agrees with polymer melt stress relaxation data. By combining this simple physical picture with our model relaxation integral equation, we deduce the molecular weight dependence of the zero-shear viscosity and the diffusion coefficient. The results indicate that the molecular weight and concentration exponents depend on the spatial dimension d and the chain fractal dimension d_f (i.e., excluded volume and chain stiffness). Results similar to the reptation model are recovered in $d = 4$ dimensions, and the classical Rouse theory[18] is obtained as $d \rightarrow \infty$ since the chains are no longer entangled in this extreme limit. We also address the physical basis of entanglement so as to obtain a better description of the concentration dependence of η_0 and D. This analysis indicates that the chain cross-sectional area is a fundamental parameter in determining the physical properties of polymer melts (i.e., short-range repulsive forces play a dominant role, as is the case in liquid crystals and simple liquids).

2. Integral Equation Approach to Relaxation in Condensed Materials

Following the standard statistical mechanical approach to relaxation,[7] we model a material as an isolated Hamiltonian (constant energy) dynamical system, which is initially at thermodynamic equilibrium. The relaxation function $\Psi(t)$, describing the self-correlation of an observable property (e.g., stress relaxation) over a time t, can be shown to satisfy the integral equation[7]

$$\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} = -\int_0^t K(|t-\tau|)\,\Psi(\tau)\,\mathrm{d}\tau \tag{2.1a}$$

$$\Psi(t<0) = 0, \quad \Psi(0) = 1 \tag{2.1b}$$

This integral equation has the requisite generality for describing relaxation in condensed materials, but calculation of the memory kernel $K(|t-\tau|)$ is difficult for physical systems of interest.

Although there is little hope of an exact calculation of $K(|t-\tau|)$ for a condensed material, we can develop models of the memory kernel that can be tested against experiment. Berne et al.[19] have demonstrated the power of this semiempirical approach, and we follow this strategy to deduce a memory kernel that is tailored to describe relaxation in condensed disordered materials. The modeling addresses two aspects of a condensed material that are considered fundamental in determining the observed relaxation, material inhomogeneity and cooperativity of molecular movement. The applications-oriented reader may wish to proceed to section 2B where the solutions of the model integral equation (eq 2.7) are summarized and compared to standard empirical relaxation functions. Specific modeling of integral equation parameters is considered in section 3.

A. Material Inhomogeneity and Generalized Model Memory Kernel. Symmetry arguments are helpful in narrowing the field of possible memory kernels to a manageable class appropriate for condensed matter relaxation. An approximate, but useful, generalization of (2.1) is introduced to describe relaxation in inhomogeneous materials.

The symmetric [$K(t,\tau) = K(\tau,t)$] translation kernel $K(|t-\tau|)$ reflects analytical symmetrices of Hamilton's equations. Specifically, the integral equation (2.1) is invariant[20] under a time translation $t \rightarrow t + a$ and under time reversal $t \rightarrow -t$ when the kernel has the special "time-translation" form $K(|t-\tau|)$. These symmetries are linked to conservation laws of the dynamical system so we must avoid the indiscriminate breaking of analytic symmetries in our modeling of the memory kernel. However, a paradox is obtained when we try to reconcile these analytical symmetries with experiment.

A small class of empirical functions[21-25] $\Psi(t)$ is found to describe relaxation in a wide range of condensed materials, and this observation has led to suggestions of "universality" in the dynamical response of condensed disordered materials.[21,25] For example, stretched exponential relaxation, $\Psi(t) \sim \exp(-t^{1-\beta})$ with $0 < \beta \leq 1$, approximates the response at long times for many materials and types of perturbation, *including polymer melt stress relaxation in the transition and terminal regimes* (see section 3).

Our initial interest in stretched exponential type relaxation was stimulated by the theoretical difficulty in reconciling the exact (2.1) with the observed stretched exponential stress relaxation in concentrated polymer solutions. At first, we concluded that a time-translation kernel $K(|t-\tau|)$ did not exist, which was consident with a stretched exponential $\Psi(t)$ at long times. The mathematical difficulty is illustrated by observing that a stretched exponential $\Psi(t)$ solution of (2.1a) corresponds to a memory kernel

$$K(t,\tau) = \delta(t-\tau)\,\Omega(\tau), \quad \Omega(\tau) \sim \tau^{-\beta} \tag{2.2}$$

where δ is a delta function. It would *appear* that the fundamental time-translation symmetry of the memory kernel is *broken* in phenomenological models employing a time-dependent rate[22-24] $\Omega(\tau)$ as in (2.2).

The modeling of polymer melt stress relaxation in section 3 provides insight into the *apparent* breaking of the time-translation symmetry of the empirical memory kernel (2.2). In section 3 we consider stress relaxation in a polymer melt to occur by the internal diffusion of clusters. The continuous distribution of relaxation times associated with the cluster size distribution leads to a memory kernel that is consistent with (2.2) for the long time decay of the relaxation function $\Psi(t)$. The apparent time-dependent rate in (2.2) for long times is found to be a power law $\Omega(\tau) \sim \tau^{-\beta}$ with an index β in the interval $0 \leq \beta < 1$, where the specific value of β depends on the geometrical type (topological dimension) of cluster introduced in the modeling. Each cluster is assumed to relax according to an exponential decay so that the modeling is consistent with the time-translation memory kernel in (2.1a). Thus, *averaging* over a continuous distribution of relaxation times can lead to a relaxation function $\Psi(t)$ whose long-time behavior is *mimicked* by the time-dependent rate in (2.2).

We should clarify that the term cluster in the discussion above refers not only to density fluctuations but to spatial variations in the extent of dynamical correlations within a material. For example, the extent of polymer chain entanglement in concentrated solutions of long polymer chains can be nonuniform where some regions of space are more "tangled up" at a given time than others. This inhomogeneity in the dynamical correlations, which we assume is long-lived on the time scale of stress relaxation, necessitates that groups of chains (clusters) move together, leading to a distribution of relaxation times associated with the cluster size distribution. Such a dynamical inhomogeneity is compatible with a large-scale uniformity of density in concentrated polymer solutions. Direct observation of entanglement clusters should be possible in semidilute entangled polymer solutions where correlated groups of chains can diffuse in isolation. In fact, semidilute entangled polymer solutions exhibit anomalous scattering at small wave vector and a "slow" diffusive mode in photon correlation spectroscopy, which has been interpreted in terms of "transient clusters of loosely entangled chains".[26,27] "Clustering" has also been suggested to explain "anomalous" light scattering in glassy liquids as the glass transition is approached.[28]

Our emphasis on the inhomogeneity of concentrated polymer solutions is contrasted with dynamical mean-field models (e.g., reptation model[2,3]) of polymer solution dynamics in which a polymer solution is assumed to be a *uniform effective medium.* These dynamical mean-field models lead to an exponential relaxation in the terminal regime[4] because they provide no mechanism for generating a dense spectrum of relaxation times. The observation of nonexponential stress relaxation in the terminal regime of concentrated polymer solutions (see section 3) suggests that dynamical mean-field theories are inadequate. Schweizer has recently introduced a promising mode-coupling theory, which seeks to avoid the dynamical mean-field approximation.[29] Perico and Freed[30] comment on the consequences of dynamical mean-field approximations on polymer solution dynamics.

The assumption of an exponential cluster relaxation in section 3, is an oversimplification that is unacceptable when we consider relaxation in amorphous polymer solids and other condensed disordered materials. Although our applications in section 3 only briefly refer to relaxation in polymer solids, we take this opportunity to further develop our integral equation approach to relaxation.

The time-dependent rate $\Omega(\tau)$ in (2.2) mimics the distribution of clustering in a condensed material as indicated in section 3. More generally we introduce an *approximate* relaxation integral equation for inhomogeneous materials

$$\frac{\mathrm{d}\Psi}{\mathrm{d}t} \approx -\int_0^t K(t,\tau)\,\Psi(\tau)\,\mathrm{d}\tau \tag{2.3a}$$

$$K(t,\tau) = K_0(|t-\tau|)\,\tau^{-\beta}, \quad 0 \le \beta < 1 \tag{2.3b}$$

where β (see section 3) models material inhomogeneity and $K_0(|t-\tau|)$ is interpreted as a memory kernel for a cluster relaxation mode. As a simple specific example we could consider the dynamics of a single Rouse chain (see section 3) where $K_0(|t-\tau|)$ corresponds to a delta function $\delta(t-\tau)$ weighted by a Rouse relaxtion rate Ω_k.[30] Dynamical motions of clusters of chains are necessarily correlated due to excluded-volume interactions, and we anticipate that the generally unknown $K_0(|t-\tau|)$ for the cluster relaxation modes could reflect a dynamical slowing down due to interchain coupling within a cluster, intrachain self-interaction and cluster–cluster interactions.[31,32] To make progress in modeling $K_0(|t-\tau|)$ from a general perspective, we again return to an examination of analytical symmetries of the memory kernel and their implications.

Relaxation functions for condensed materials exhibit regularities that can be traced to nontrivial symmetries of the memory kernel. For example, relaxation functions for condensed materials are often observed to be approximately invariant[1,33] in shape when temperature or pressure is varied, aside from a temperature-dependent redefinition of the relaxation time scale. This is an extraordinary symmetry. An exact invariance of the relaxation function shape with a change in relaxation time can be shown to be equivalent (see Appendix A) to a memory kernel that has time-dilation symmetry

$$K(st,s\tau) = s^{\gamma}K(t,\tau) \tag{2.4}$$

where γ is a constant. The class of memory kernels that has the property (2.4) is very limited, and thus we have a clue on how to proceed with modeling the memory kernel.

Feller[8] introduced a general theory of "return to equilibrium" in dynamical processes governed by a random evolution whose increments form a stationary random process. The motivation for modeling the dynamics of a condensed material at equilibrium by such a stochastic process is discussed by Uhlenbeck.[34] Here we stress only the more direct mathematical connections between the classical statistical mechanical approach to relaxation[7] and Feller's "renewal" theory[8] and its generalizations.[9–11]

Integrating both sides of the relaxation integral equation (2.1a) from 0 to t yields a "renewal equation"[8,9,35,38]

$$\Psi(t) = 1 - \int_0^t R_0(t-\tau)\,\Psi(\tau)\,\mathrm{d}\tau \tag{2.5a}$$

$$R_0(t) = \int_0^t K_0(\tau)\,\mathrm{d}\tau \tag{2.5b}$$

Except for an additive constant, which we ignore, the asymptotic behavior of the "renewal rate" $R_0(t)$ is governed by a limit theorem[8,10,39–41]

$$R_0(\tau) \sim \tau^{\phi-1}, \quad \tau \to \infty, \quad 0 < \phi \le 1 \tag{2.6a}$$

Equation 2.5b implies that $K_0(\tau)$ scales as

$$K_0(\tau) \sim \tau^{\phi-2}, \quad \tau \to \infty, \quad 0 < \phi \le 1 \tag{2.6b}$$

which is consistent with the dilation symmetry observed experimentally [see (2.4)]. Combining the renewal theory result (2.6b) with (2.3) yields a *model* integral equation for relaxation in condensed disordered materials

$$\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} \approx -\int_0^t K(t,\tau;\phi,\beta)\,\Psi(\tau)\,\mathrm{d}\tau, \quad \Psi(0) = 1 \tag{2.7a}$$

$$K(t,\tau;\phi,\beta) = \Omega_0(t-\tau)^{\phi-2}\tau^{-\beta}/\Gamma(\phi-1), \quad 0 < \phi \le 1, \quad 0 \le \beta < 1 \tag{2.7b}$$

where the gamma function $\Gamma(\phi-1)$ is introduced as a normalization factor so that

$$\lim_{\phi\to 1^+} K(t,\tau;\phi,\beta) = \Omega_0\delta(t-\tau), \quad \beta = 0 \tag{2.8}$$

The limit (2.8) is discussed by Douglas[42] where (2.7a) arises in connection with the partition function of a polymer subject to geometrical constraints.[6,42–44] The choice of the prefactor Ω_0 in (2.7b) is motivated by the analogy between (2.7) and the integral equation describing a surface-interacting polymer[42] where Ω_0 is the analogue of the polymer–surface coupling constant (see section 2B for further discussion of this assumption).

It is emphasized that our cluster model does not provide a unique "explanation" of the time-dependent rate $\Omega(\tau) \sim \tau^{-\beta}$ in (2.2). An alternate approach is to consider relaxation in a disordered material to occur as an "inhomogeneous dynamical process" such that the rate at which an observed process occurs is nonuniform. In "defect diffusion" models,[46] for example, the relaxation process is actuated by a second random process, leading to a time-dependent rate $\Omega(\tau)$ of the form (2.6a).

B. Solution of the Model Relaxation Integral Equation. The solutions of (2.7a) with the memory kernel (2.7b) decay monotonically where the presence of memory ($\phi \neq 1$, $\beta \neq 0$) yields a long-time tail rather than the simple exponential decay of classical relaxation theories. Next, we examine some specific solutions of the integral equation (2.7) and then give a general solution.

For $\phi = 1$ and $\beta = 0$ a simple exponential decay for $\Psi(t)$ is obtained from (2.7)

$$\Psi(t;\beta=0,\phi=1) = \exp(-\Omega_0 t) \tag{2.9a}$$

while $\beta = 0$ and $\phi \neq 1$ produces the Mittag–Leffler relaxation function[6,42,45]

$$\Psi(t;\beta=0,\phi) = \sum_{k=0}^{\infty}[-z_\Omega(\beta=0)]^k/\Gamma(1+k\phi), \quad 0 \le \phi \le 1 \tag{2.9b}$$

$$z_\Omega(\beta=0) = \Omega_0 t^\phi \tag{2.9c}$$

(2.9b) evidently reduces to (2.9a) for $\phi \to 1^+$. Equation 2.9b is more familiar in the frequency domain where it is known as the Cole–Cole function[22] and in mechanical relaxation context (2.9b) corresponds to a power law creep function.[47,48] With $\phi = 1$ and $\beta \neq 0$ a stretched exponential is obtained[21,24]

$$\Psi(t;\beta,\phi=1) = \exp[-\Omega_0 t^{1-\beta}/(1-\beta)] \tag{2.9d}$$

The general solution of (2.7) equals

$$\Psi(t;\phi,\beta) = \sum_{k=0}^{\infty} a_k(\phi,\beta)[-z_\Omega(\phi,\beta)]^k, \quad 0 < \phi \le 1, \quad 0 \le \beta < 1 \tag{2.10a}$$

$$a_k(\phi,\beta) = \prod_{m=0}^{k}\Gamma[1+m\hat{\phi}-\phi]/\Gamma(1+m\hat{\phi}) \tag{2.10b}$$

$$\hat{\phi} = \phi - \beta, \quad \hat{\phi} > 0 \tag{2.10c}$$

$$z_\Omega(\phi,\beta) = \Omega_0 t^{\hat{\phi}} \equiv [t/\tau^*(\phi,\beta)]^{\hat{\phi}} \tag{2.10d}$$

$$\tau^*(\phi,\beta) = \Omega_0^{-1/(\phi-\beta)} \tag{2.10e}$$

Asymptotic properties of this Koutecky-type function (2.10) are summarized by Oldham and Spanier.[49] For $0 < \hat{\phi} < 1$ the relaxation function Ψ has the asymptotic behavior

$$\Psi(t;\phi,\beta) \sim C_4 t^{-\hat{\phi}}, \quad t \gg \tau^*(\phi,\beta) \tag{2.11a}$$

and the associated decay current $I(t) = [-\mathrm{d}\Psi/\mathrm{d}t]$ scales as

$$I(t) \sim C_5 t^{\hat{\phi}-1}, \quad t \ll \tau^*(\phi,\beta) \tag{2.11b}$$

$$I(t) \sim C_6 t^{-(\hat{\phi}+1)}, \quad t \gg \tau^*(\phi,\beta) \tag{2.11c}$$

where C_4, C_5, C_6 are constants. Jonscher[25,50] has shown that the relaxation decay in (2.11) is observed in a variety of materials. The qualitative form of (2.10) in the frequency domain resembles the Havriliak–Negami function, which is widely used to correlate relaxation data.[51]

Another noteworthy property of (2.7) is the renormalization of the relaxation time as a consequence of memory. In the absence of memory $\Psi(t)$ is a function of $\Omega_0 t$ and the relaxation time τ is given by $\tau = \Omega_0^{-1}$. From (2.10e) we see that the relaxation time of a system with memory involves a power law relation between τ and Ω_0. A "renormalization" of the relaxation time as a consequence of memory effects as in (2.10e) was first obtained in the Scher and Montroll[51] theory of transient photocurrent decay in disordered materials where a decay current $I(t)$ of the form (2.11) is also obtained. Ngai et al.[21] have enumerated many physical systems which support the prediction of a rescaling of the relaxation time as a consequence of memory persistance as measured by the empirical index β. These observations lend support to the assumed form of the prefactor in (2.7b).

The memory kernel (2.7b) depends on two parameters ϕ and β which describe how relaxation is altered from classical relaxation models. The "evolution rate" $\Omega(\tau) \sim \tau^{-\beta}$ in (2.3) is associated with material inhomogeneity so that β is a dimensionless measure of material disorder. Explicit estimates of β are given in the next section. The exponent ϕ is interpreted as a measure of the cooperativity of local dynamics, a classical example of which is the self-diffusion of a sphere in a viscous fluid.[52] The motion of the sphere induces correlations in the surrounding medium with a "penetration depth" that increases as the square root of the solvent viscosity.[52] The damping of these disturbances is controlled by vorticity diffusion[52] and leads to a power law memory kernel as in (2.6b) along with power law relaxation as in (2.11e). We anticipate that the diffusive damping of local disturbances is a common mode of relaxation in condensed materials where molecular motions are necessarily correlated.

3. Application of the Relaxation Model to Polymer Melt Dynamics

In 1913 Hatschek[53] observed that the damping of vibrations in condensed disordered materials, such as colloid solutions, depends strongly on the frequency of excitation. Damping of acoustic waves in disordered solids as a function of frequency was also noted by Thomson,[54] and a similar frequency-dependent response has been observed for many viscoelastic materials subject to a variety of perturbations.[1,53b]

Maxwell[12] and Gemant[13] suggested that the frequency-dependent viscosity of complex fluids and solids implied that the substituent molecules are capable of two types of motion depending on the time scale. At short times or high frequencies the molecules are displaced elastically in a fashion similar to a crystalline solid, but at longer times or low frequencies there is viscous flow under a sustained stress. We now apply this classical conceptual model of a viscoelastic material to describe transport properties of concentrated polymer solutions and melts, taking into account the dynamic inhomogeneity of the medium. Readers more interested in the molecular weight dependence of concentrated polymer solution transport properties may which to proceed first to section 3C.

A. "Glassy Relaxation". The structure of a liquid below its melting point T_m is expected to be governed by a dynamical equilibrium between regions of disorder and clusters of relative order.[15,28,55] Although these cluster structures generally fall short of propagating into the full translational order of the crystalline phase for modest cooling, the existence of these transient clusters can be expected to modify the transport properties of these liquids considerably.

The general philosopy of our calculations is to model "complex" liquids, and other such amorphous materials, as containing an ensemble of clusters.[6,47] The response of this ideal inhomogeneous material to a disturbance involves an *averaging* over the cluster distribution.[47] We treat the short-time elastic response of complex fluids by modeling the clustering and the relaxation process.

At first, we neglect cooperative motion memory effects (i.e., $\phi = 1$) and consider only the relaxation function of a cluster of spatial extent L

$$\Psi(t) = \exp[-t/\tau(L)] \tag{3.1}$$

where $\tau(L)$ is the cluster relaxation time. Assuming that relaxation occurs by internal diffusion of the clusters[26c] and that the Einstein relation between the diffusion coefficient and the friction coefficient holds, then by dimensional analysis we have

$$\tau(L) \sim fL^2/k_BT \tag{3.2}$$

where T is temperature and k_B is Boltzmann's constant. Further, we define an average relaxation time $\tau_{0g} = fL_0^2,/k_BT$ [see (3.2)] where L_0 is an average cluster size. The short-time response of an inhomogeneous medium should weight the response of regions having a relaxation time less than or equal to the average value τ_{0g}. The response of the large clusters lags behind the small clusters whose response time (relaxation time) is shorter.[56]

The structure of disordered condensed materials is often modeled in terms of "defects". Models of this kind have become highly developed in the modeling of crystalline materials (disclinations, dislocations, point defects, etc., ...),[14,15,57] and Rivier,[14] Vlasov,[15] and Nelson et al.[16] have recently stressed the importance of *defect lines* in amorphous materials. Rivier calls these vortexlike structures "disclination lines" in structural glasses and "frustration lines" in spin glasses.[14] The defect line models[14,16] vary in detail, but the aspects that are important for our modeling of relaxation are rather model independent: the defect lines have a topological dimension of one and have a distribution of lengths. It is supposed that the energy of these defect structures is proportional to their length (as in disclination lines in crystals[57]) and that Boltzmann's law governs the length distribution $\exp(-L/L_0)$ where the mean defect line length, L_0, reflects model parameters relevant to a particular disordered material. Glassy stress relaxation is assumed to occur by the internal diffusion of these "polymeric" clusters in much the same fashion as stress relaxation in dilute polymer solutions.[26c] The presence of clusters, even in low molecular weight viscoelastic fluids, should be evidenced by a slow diffusive ($\Gamma \sim q^2$) mode in photon correlation spectroscopy and by an excess Rayleigh scattering.[28]

The glassy stress relaxation function $\Psi_g(t)$ is calculated as an average of the single cluster relaxation function (2.1) with respect to the distribution of cluster sizes. The Boltzmann distribution of cluster sizes of length L implies

$$\exp(-L/L_0) = \exp[-(\tau/\tau_{0g})^{1/2}] \tag{3.3a}$$

and averaging this distribution with the cluster relaxation function (3.1) yields

$$\Psi_g(t) = \int d\tau \exp(-t/\tau) \exp[-(\tau/\tau_{0g})^{1/2}] \tag{3.3b}$$

which defines a LeRoy function.[58,59] The asymptotic dependence of $\Psi_g(t)$ is deduced by steepest descent as

$$\Psi_g(t) \sim \exp(-ct^{1/3}), \quad t \to \infty \tag{3.4a}$$

where the definition of c absorbs τ_{0g} and other parameters. For a uniform material the averaging as in (3.3b) leads to the exponential form (3.1).

A model expression for the glassy stress relaxation function $G_g(t)$ is obtained by relating the cluster model expressions (3.1) and (3.4a) to the model integral equation (2.7). This correspondence implies

$$G_g(t) = G_g{}^\circ\Psi_g[t/\tau_g{}^*;\phi_g{=}1,\beta_g(T)] = \\ G_g{}^\circ \exp[-(t/\tau_g{}^*)^{1-\beta_g(T)}] \tag{3.4b}$$

$$\beta_g(T{\to}\infty) = 0, \quad \beta_g(T{\approx}T_g) = 2/3 \tag{3.4c}$$

where the glassy shear modulus $G_g{}^\circ$ is typically on the order[1,60] of $G_g{}^\circ \sim O(10^9\text{–}10^{10})$ dyn/cm^2. The integral equation (2.7) is employed below to estimate the glassy relaxation time $\tau_g{}^*$.

The effective exponent $1 - \beta_g(T)$ of the stretched exponential (3.4b) in glasses generally decreases from a behavior like (3.1) at high temperatures toward a behavior like (3.4a) near the glass transition.[61] This same trend is observed for relaxation in spin glasses where $\beta_g \approx 0$ at high temperatures and $\beta_g \approx {}^2/_3$ near the spin–glass transition.[62] Experimental estimates[63] of β_g for polymers near the glass transition are rather consistent with the cluster model estimate $\beta_g = {}^2/_3$ in (3.4c). For example, a fit[21b] to polystyrene melt creep data obtained by Plazek indicates $\beta_g = 0.65$.

Values of β_g closer to ${}^1/_2$ are sometimes observed in small-molecule glasses,[64] which suggests that our simple linear defect model is not correct for these materials. It is perhaps relevant that Kantor et al.[31] suggest that certain small-molecule glass-forming liquids above their glass transition temperatures contain sheetlike (two-dimensional) surfaces rather than linear defects. Generalization of (3.3) to two-dimensional defect structures[15,31] yields a value $\beta_g = {}^1/_2$. It should also be appreciated that flow relaxation processes are not well separated from the glassy response in small-molecule liquids and the apparent stress-relaxation exponent β_g for small-molecule liquids could reflect an average of the glassy and flow relaxation processes. In high molecular weight polymers the flow relaxation is shifted to much longer times so that this mixing of relaxation processes is not a complication.

Now if we use the argument above to specify the glass transition parameter β_g in our relaxation equation (2.10e), we see that the glassy relaxation time $\tau_g{}^*(\phi_g{=}1,\beta_g)$ varies with temperature through the exponent $\beta_g(T)$. At high temperatures we expect a classical Arrhenius temperature dependence of the glassy relaxation time $\tau_g{}^*(\phi_g{=}1;\beta_g{=}0)$[65–67]

$$\tau_g{}^*[\phi_g{=}1,\beta_g(T{\to}\infty){=}0] = \tau_g{}^\infty \exp(E_a/k_BT) \tag{3.5a}$$

where $\tau_g{}^\infty$ is a relaxation time prefactor reflecting the local segmental motion[65] and E_a is the flow activation energy.[66,67] At lower temperatures (2.10e) and (3.4b) imply

$$\tau_g^*(\phi_g{=}1,\beta_g(T)) \sim (\tau_g^{\infty})^{1/[1-\beta_g(T)]} \exp\{E_a/k_BT[1-\beta_g(T)]\} \tag{3.6}$$

Defining a temperature-dependent linear interpolation between the limits $\beta_g(T{\rightarrow}\infty) = 0$ and $\beta_g(T{=}T_g) = \beta_g^*$ [see (3.4c)] gives

$$\beta_g(T) = \beta_g^*[1-(T-T_g)/T] \tag{3.7}$$

where $\beta_g^* \approx {}^2/_3$. Equation 3.7 employs the tentative assumptions that (3.4a) holds at the glass transition temperature, that simple exponential relaxation is obtained at "high" temperatures ($T{\rightarrow}\infty$), and that β_g depends linearly on T. These assumptions imply [insert (3.7) in (3.6)]

$$\tau_g^*(\phi_g{=}1,\beta_g(T)) \propto \exp[(E_a/k_B(T-T_\infty))], \quad T_\infty = \beta_g^*T_g \tag{3.8a}$$

which corresponds to the empirical Vogel equation.[17] (3.8a) is a successful empirical expression for $\tau_g^*(T{>}T_g)$ in glasses where E_a and T_∞ are adjusted as free parameters.

The simple approximation (3.7) for $\beta_g(T)$ is adequate for a rough estimation of T_∞ and the temperature dependence of τ_g^*. Actually, we expect to recover simple exponential decay and an Arrhenius dependence of τ_g^* on temperature at some *finite* temperature $T_A > T_g$ where T_A corresponds to a point at which deviation from Arrhenius behavior first occurs (see below). Heuristically, we expect T_A to lie near the melting temperature T_m of crystallizable materials since this is a natural point for the energetics to favor clustering.[55] For polymers having a T_g near room temperature, the melting temperature T_m is often 100–200 °C above T_g[68] (see McKenna[69] for the definition of T_g). A generalization of (3.7) in which $\beta_g(T)$ vanishes at T_A and is linear in T is given by

$$[\beta_g^* - \beta_g(T)]/\beta_g^* = (T - T_g)/\Delta T \tag{3.8b}$$

$$\Delta T = T_A - T_g, \quad T_g < T < T_A \tag{3.8c}$$

$$\beta_g(T{>}T_A) = 0 \tag{3.8d}$$

Inserting (3.8b) into (3.6) implies a generalization of the Vogel equation, which we anticipate to be more accurate in correlating experimental data.[70] Application of (3.8), however, requires an estimate of the critical temperature T_A.

Adam and Gibbs[71] summarize estimates of T_∞/T_g (T_∞ is identified with a parameter T_2[71,72]) and observed the ratio to be nearly *universal* for 15 glass-forming liquids

$$T_\infty/T_g \approx 0.8\text{–}0.7 \tag{3.9a}$$

and a similar ratio was obtained by Bestul and Chang[73] from calorimetric studies. Experimental data (see also ref 74) for structural glasses agree reasonably with the rough estimate obtained from (3.8a) and (3.4a)

$$T_\infty/T_g = \beta_g^*, \quad \beta_g^* \approx 2/3 \tag{3.9b}$$

Equation 3.9b applies only in the limit $T_A \gg T_g$, and (3.6) with (3.8b) is suggested as a refinement over the Vogel expression (3.8a).

B. Comments on Sub-T_g Relaxation. For temperatures below the glass transition temperature ($T_\infty < T < T_g$) the relaxation time τ_g^* can become extremely long. An understanding of sub-T_g relaxation is essential for understanding the change ("physical aging") of physical properties in glassy materials over the long periods of time over which relaxation occurs.

The exponent β_g is expected to "stick" to the critical value ${}^2/_3$ in this regime, as in the instance of spin glass data.[75] Indeed, Lee and McKenna[76] obtain $\beta_g = 0.66$ for sub-T_g stress relaxation in epoxy networks. For a large relaxation time the expansion of the stretched exponential (3.4b) becomes a reasonable approximation so that we have

$$\Psi_g(t,T_g{<}T{<}T_\infty) \sim e^{-(t/\tau_g^*)^{1/3}} \approx 1 - (t/\tau_g^*)^{1/3} \tag{3.4b}$$

The creep function[1] $J(t)$ is slowly varying in this regime since τ_g^* is large and we obtain the approximation $J(t) \approx [\Psi_g(t)]^{-1}$ so that a power law creep with index ${}^1/_3$ is obtained

$$J(t) \approx e^{(t/\tau_g^*)^{1/3}} \approx 1 + (t/\tau_g^*)^{1/3} \tag{3.4c}$$

The power law increase of $J(t)$ with an index of ${}^1/_3$ (Andrade creep) is ubiquitous in glassy polymers[48,77] and other condensed materials such as bitumen, shellac, bread dough, amorphous sugar, and polycrystalline lead and other metals.[78-80]

For temperatures below T_∞, we still have relaxation but we anticipate that highly cooperative motions are involved, i.e., $\phi_g \neq 1$. Once ϕ_g deviates from unity, the asymptotic dependence of the relaxation function $\Psi(t;\phi_g,\beta_g)$ crosses over from stretched exponential to power law decay [see (2.10) and (2.11)], a liquid–solid transition. A transition of this kind has been observed in spin glasses,[81] and we plan to examine polymer glasses to see if this behavior is observed under general circumstances. We mention that Kolsky[82] has studied stress waves in solid polymers and observed a "universal response" consistent with $0 < \phi_g < 1$ and $\beta_g = 0$ (see Pipkin[83]), i.e., "power law solids". At the moment we have no model for the variation of ϕ_g and β_g for $T \leq T_\infty$. Further experimental and theoretical work is needed to obtain insight into sub-T_g relaxation and the discussion below is confined to $T > T_g$.

C. Viscous Flow. The Amoeba Model. Relaxation in concentrated high molecular weight polymer fluids exhibits two distinct relaxation processes. At short times a glassy "transition region" is observed, followed by a rubbery "terminal region". In this section we address relaxation in the terminal regime.

At times longer than the initial glassy response ($t > \tau_g^*$), it is possible for clusters within a stressed inhomogeneous material to rearrange themselves (i.e., "flow"). Obviously, larger regions should respond more sluggishly than smaller ones because of their greater relaxation time [see (3.2)]. The observed response reflects an averaging over environments as in the short-time glassy response discussed in section 3A. However, in the flow relaxation process the clusters are assumed to be domains of volume V rather than one-dimensional defect structures. Specifically, we have in mind "swarms"[26c] of entangled chains in the context of concentrated polymer solutions (see section 3D). Assuming that the energy of a cluster increases linearly with its volume, we obtain a Boltzmann distribution function $\exp(-V/V_0)$ for the cluster volumes where V_0 is the average cluster volume.

The observed flow relaxation function $\Psi_F(t)$ is an average of the local relaxation function $\exp[-t/\tau(V)]$ with respect to the exponential distribution of cluster volumes

$$\Psi_F(t) = \int d\tau \exp[-t/\tau(V)] \exp(-bV/V_0) \tag{3.10a}$$

Defining an average flow relaxation time $\tau_{0F} \propto fV_0^{2/d}/k_BT$

[see (3.2)] with d the spatial dimension gives

$$V/V_0 \equiv (\tau/\tau_{0\mathrm{F}})^{d/2} \tag{3.10b}$$

and inserting (3.10b) into (3.10a) yields a d-dimensional generalization of (3.1)

$$\Psi_{\mathrm{F}}(t) = \int \mathrm{d}\tau \exp[-t/\tau] \exp[-(\tau/\tau_{0\mathrm{F}})^{d/2}] \tag{3.10c}$$

Steepest descent implies the asymptotic dependence

$$\Psi_{\mathrm{F}}(t) \sim \exp(-g t^{d/(d+2)}), \quad t \to \infty \tag{3.11a}$$

where the g parameter is a function of the local friction f (and thus τ_g^*) and V_0 (see below). For a homogeneous material the observed relaxation function $\Psi_{\mathrm{F}}(t)$ is dominated by an exponential dependence on time as in (2.1). The argument to obtain (3.11a) arises in many physical contexts.[84]

From (3.11a) we obtain the model integral equation (2.7) parameters $\phi_{\mathrm{F}} = 1$ and $\beta_{\mathrm{F}} = 2/(d + 2)$ in the entangled regime so that the decay of the relaxation modulus $G(t)$ off the rubbery plateau becomes [see (3.11f) for an explicit expression for $G_{\mathrm{F}}(t)$]

$$G_{\mathrm{F}}(t) = G_{\mathrm{N}}\Psi_{\mathrm{F}}[t/\tau_{\mathrm{F}};\phi_{\mathrm{F}}=1,\beta_{\mathrm{F}}=2/(d+2)] \text{ (entangled limit)} \tag{3.11b}$$

The plateau modulus G_{N} prefactor in (3.11b) generally has a magnitude[1] on the order of 10^6 dyn/cm^2 in a polymer melt (see Appendix B), and the average flow relaxation time τ_{F} is discussed below. The theoretical prediction $\beta_{\mathrm{F}}(d{=}3) = 0.4$ agrees well with terminal relaxation data where $\beta_{\mathrm{F}} \approx 0.45$ is obtained for a polystyrene melt.[21b] Terminal stress relaxation data for polystyrene melts obtained by Tobolsky et al.[35d] indicates $\beta_{\mathrm{F}} \approx 0.4$. Ngai and Plazek[85a,c] find $\beta_{\mathrm{F}} = 0.43$ for polyethylene and $\beta_{\mathrm{F}} = 0.42$ for hydrogenated polybutadiene. The observed stress-relaxation function $G(t)$ is taken to be the sum of the glassy contribution $G_g(t)$ in (3.4) and the flow contribution $G_{\mathrm{F}}(t)$.

Measurement of the creep compliance provides further information on the stress relaxation of concentrated polymer solutions. The equilibrium compliance J_e times the zero-shear viscosity η_0 is proportional to the average terminal stress relaxation time,[1] τ_{F}

$$J_e\eta_0 = \int_0^\infty tG(t/\tau_{\mathrm{F}})\,\mathrm{d}t \Big/ \int_0^\infty G(t/\tau_{\mathrm{F}})\,\mathrm{d}t \tag{3.11c}$$

Performing the integral in (3.11c) with $G(t/\tau_{\mathrm{F}})$ defined by (3.11a) gives

$$J_eG_{\mathrm{N}} = [d/(d+2)]\Gamma[2(d+2)/d]/\Gamma^2[(d+2)/d] \tag{3.11d}$$

The product J_eG_{N} provides a dimensionless measure of the "shape" of the relaxation function. For large d this dimensionless ratio approaches unity and in three dimensions J_eG_{N} equals

$$J_eG_{\mathrm{N}}(d{=}3) = (3/5)\Gamma(10/3)/[\Gamma(5/3)]^2 = 2.046 \tag{3.11e}$$

as noted previously[35] for an empirical index $\beta_{\mathrm{F}} \approx {}^2/_5$. The reptation model predicts $J_eG_{\mathrm{N}} = {}^6/_5$ instead of the single exponential estimate $J_eG_{\mathrm{N}} = 1$, the correction coming from the sum over relaxation modes.[91] Experimentally J_eG_{N} is about 2.4 for fairly monodisperse entangled polymers, in qualitative agreement with (3.11e).[92] The large experimental deviation of J_eG_{N} from unity indicates that dynamical mean-field models, such as the reptation model, give a rather inaccurate description of stress relaxation in concentrated polymer solutions. We next turn to the model predictions for the concentration and molecular weight dependences of G_{N} and τ_{F}.

The plateau modulus[1] G_{N} is a quasi-equilibrium analogue of the shear modulus of rubber elasticity. In Appendix B the concentration c dependence of G_{N} is estimated as

$$G_{\mathrm{N}} \sim c^{(d+1)/(d-1)} \tag{3.12a}$$

which agrees well with the experimental variation of the plateau modulus at high concentrations[1]

$$G_{\mathrm{N}} \sim c^2, \quad d = 3 \tag{3.12b}$$

In semidilute entangled solutions this argument needs to be generalized (see Appendix B).

The Rouse model provides a reasonable phenomenological model of concentrated unentangled polymer solutions. Matching $G_{\mathrm{F}}(t)$ to the Rouse result in the absence of entanglement allows the modeling of the molecular weight dependence of τ_{F} on the basis of the integral equation result (2.10e). Rouse model predictions[1,17] for $G_{\mathrm{R}}(t)$ and τ_{F} are schematically reviewed and combined with (2.10e) and the estimate $\beta_{\mathrm{F}} = 2/(d + 2)$ in (3.11b) to deduce the molecular weight dependence of τ_{F} for entangled chains. The crossover from Rouse to entangled chain relaxation is discussed in the next section.

The molecular weight dependence of the Rouse relaxation times τ_{R} can be understood heuristically from (3.2) where we take L, the size of the diffusing object, equal to the polymer root-mean-square end-to-end distance $\langle R^2\rangle^{1/2}$ to obtain the relaxation time τ_{R} as

$$\tau_{\mathrm{R}} \sim f\langle R^2\rangle/k_{\mathrm{B}}T \tag{3.13a}$$

This result is obtained also in the formal theory[1,17] and is convenient for generalizing our considerations to chains with excluded volume and the stiffness. The friction coefficient f is proportional to the number of chain segments in the Rouse model (the molecular weight M) and τ_g^* so that τ_{R} scales as

$$\tau_{\mathrm{R}} \sim \tau_g^* M\langle R^2\rangle \tag{3.13b}$$

The stress relaxation function $G_{\mathrm{R}}(t)$ in the Rouse model[1,17] involves a sum over n Rouse modes corresponding to the internal normal coordinates of the polymer chain

$$G_{\mathrm{R}}(t) = G_{\mathrm{R}}\sum_{k=1}^{n} e^{-t/\tau_{\mathrm{R},k}} \tag{3.13c}$$

$$G_{\mathrm{R}} = cRT/M, \quad \tau_{\mathrm{R},k} \cong \tau_{\mathrm{R}}/k^2, \quad \tau_{\mathrm{R}} \equiv \tau_{\mathrm{R},1} \tag{3.13d}$$

The terminal (longest) relaxation time τ_{R} scales with molecular weight according to (3.13b), and the Rouse relaxation times $\tau_{\mathrm{R},k}$, corresponding to large k and small-scale chain motions, decrease at a geometric rate [see (3.13d)] so that $G_{\mathrm{R}}(t)$ is dominated at long times by a single exponential[1]

$$G_{\mathrm{R}}(t) \approx G_{\mathrm{R}}e^{-t/\tau_{\mathrm{R}}}, \quad t \geq \tau_{\mathrm{R}} \tag{3.13e}$$

Determining the viscosity and other transport properties by integrating (3.13e) instead of the exact (3.13c) gives rise to some inaccuracy in constants of proportionality, but the scaling of transport properties with molecular weight is unaffected. The single-mode approximation (see also ref 21) is adopted here to discuss the molecular weight scaling for unentangled and entangled chains at high concentration. Discussion of dilute-solution polymer dynamics is strictly avoided because of complications due to hydrodynamic interactions.

The collective stress relaxation of an entangled fluid of high molecular weight polymers cannot be described by the single-chain Rouse stress relaxation function (3.13c) or the approximation (3.13e). We conceive that relaxation in entangled polymer solutions occurs by the diffusion of amoeba-shaped clusters of entangled chains [see section 3D for a proposed mechanism of such chain coupling] moving as collective groups over the time scale of stress relaxation. Our simple model of this cluster diffusion process led to the estimate $\beta_F = 2/(d + 2)$ in (3.12a) so that $G_F(t)$ of a highly entangled polymer solution is obtained explicitly from (3.13e) and (2.10e) as

$$G_F(t) \approx G_N \exp[-(t/\tau_F)^{1-\beta_F}] \quad \text{(entangled chains)} \qquad (3.11f)$$

A change in relaxation from exponential to stretched exponential brings about a renormalization of the Rouse relaxation time τ_R to the "entangled chain" relaxation time τ_F. The model equation (2.10e) indicates that τ_F scales as

$$\tau_F \sim \tau_R^{1/(1-\beta_F)} \sim \tau_R^{(d+2)/d} \quad \text{(entangled chains)} \qquad (3.14a)$$

The flow relaxation time τ_F evidently reduces to the Rouse relaxation time τ_R in the absence of entanglement interaction [$\beta_F = 0$; see (3.13e)]. Thirion[86] introduced a phenomenological stress-relaxation function similar to (3.11f), and Ngai and co-workers[21] have suggested a relaxation function of the form (3.11f) along with a terminal relaxation time in accord with (3.14a) where β_F is obtained empirically. Tobolsky et al.[85d] first introduced (3.11f) to describe terminal stress relaxation in polymer melts.

We obtain the molecular weight dependence implied by (3.14a) by first observing that $\langle R^2 \rangle$ typically scales as a power law

$$\langle R^2 \rangle \sim M^{2/d_f} \qquad (3.15)$$

where d_f is the chain "fractal dimension" [$d_f = 2$ (Gaussian chain), $d_f = 1$ (stiff chain)]. From (3.13b) and (3.14a) the flow relaxation time τ_F scales with molecular weight as

$$\tau_F \sim [M^{(d_f+2)/d_f}]^{(d+2)/d}, \quad d > 2 \qquad (3.14b)$$

where the chains are sufficiently long so that the molecular weight dependence of τ_g^* is not a complication. For a concentrated solution of flexible chains ($d_f = 2$) in three dimensions, τ_F has the predicted behavior (see also ref 21)

$$\tau_F \sim M^{10/3} \qquad (3.14c)$$

For chains with excluded volume we can estimate d_f by the Flory value[87] [$d_f \approx (d + 2)/3$, $2 < d < 4$], which, along with (3.14b), gives

$$\tau_F \sim M^{(8+d)/d} \qquad (3.14d)$$

Equation 3.14d reduces to $^{11}/_3$ for $d = 3$ and to the reptation value 3 for $d = 4$.

The zero-shear viscosity η_0 is obtained as an integral of the relaxation modulus $G(t)$

$$\eta_0 \equiv \int_0^\infty G(t)\, dt \approx \int_0^\infty G_F(t/\tau_F)\, dt \qquad (3.16)$$

Inserting the flow relaxation modulus, defined by (3.12a), into (3.10) yields

$$\eta_0 \sim G_N \tau_F \sim [M^{(d_f+2)/d_f}]^{(d+2)/d} (\tau_g^*)^{(d+2)/d} \qquad (3.17a)$$

where simple constants of proportionality are neglected. For a concentrated polymer solution of long flexible chains, we obtain

$$\eta_0 \sim M^{10/3}, \quad d = 3, d_f = 2 \qquad (3.17b)$$

and somewhat larger exponents are implied for chains with excluded volume and "stiff" chains

$$\eta_0 \sim M^{11/3}, \quad d = 3, d_f = 5/3 \quad \text{(swollen chains)} \qquad (3.17c)$$

$$\eta_0 \sim M^5, \quad d = 3, d_f = 1 \quad \text{(stiff chains)} \qquad (3.17d)$$

Semiflexible chains can perhaps be *roughly* modeled by taking d_f as variable according to experimental observations based on (3.15). As mentioned before, a viscosity exponent of 3.4 is commonly found in concentrated polymer solutions of flexible polymers, although a range of exponents between 3.3 and 3.7 is generally observed[1] in accordance with (3.17b) and (3.17c). Baird and Ballman[88] obtained a viscosity exponent of about 7 for charged stiff polymers, which is roughly consistent with (3.17d). An exponent close to 5 has also been reported for the stiff polymer cellulose trinitrate in butyl acetate.[89] We also observe that $G_F(t)$ in (3.12e) is predicted to be the *same* for entangled flexible and stiff polymers. Ferry[1] notes that stress relaxation in entangled DNA solutions is remarkably similar to concentrated solutions of entangled flexible polymers.

The variation of the molecular weight dependence of η_0 and τ_F with spatial dimension is reasonable. In the limit of high dimension the ideal Rouse theory is recovered,[1,17] $\tau_F \sim \tau_R \sim M^2$. Space is so open for high dimensionality that entanglement coupling has no effect. The ideal mean-field reptation model prediction[3,4] is recovered in four dimensions

$$\eta_0 \sim M^3, \quad d = 4, d_f = 2 \qquad (3.18a)$$

Recent experiments[90] measuring the viscosity of thin films report large enhancements of the viscosity in the limit of small film thickness. This qualitative effect can be understood by taking the formal limit $d \to 2^+$ in (3.17a) to obtain

$$\eta_0 \sim M^4, \quad d \to 2^+, d_f = 2 \qquad (3.18b)$$

The zero-shear viscosity is experimentally ill-defined in two dimensions, but it should be possible to measure the viscosity of thin films (thickness less than a chain radius of gyration), which can be reasonably idealized as two dimensional. The *enhancement* of entanglement effects upon lowering the dimension could be very important for describing the viscoelastic properties of polymer films, the spreading of polymer fluids on surfaces,[90c] and other phenomena involving the dynamics of polymers at interfaces. As a final point we mention that the dimensional dependence of entangled polymer solution relaxation times is very similar to that found in Kantor et al.'s calculations[31] for flexible self-avoiding tethered sheets where the terminal relaxation time in $d = 3$ scales as $M^{3.6}$ and as M^4 in the limit $d \to 2^+$ [see (3.17) and (3.18)].

D. Crossover between Rouse and Entangled Limits. Entanglement effects modify the chain dynamics from the ideal Rouse theory. We anticipate a crossover from the simple exponential relaxation of the Rouse theory to the "entangled" stretched exponential relaxation as given in (3.11). This crossover parallels the variation of the glassy relaxation modulus $G_g(t)$ in (3.4b) where simple exponential decay is obtained at high temperatures and a stretched exponential decay is obtained as the temperature is lowered to near the glass transition temperature.

Before modeling the crossover from Rouse to entangled dynamics, we briefly review the physical situation in different concentration regimes in order to motivate the introduction of an "entanglement coupling parameter". At low concentrations the Rouse theory in conjunction with hydrodynamic and excluded-volume interactions provides a good approximate model of polymer solution dynamics.[1] At the onset of the semidilute regime, transport properties are observed to scale with concentration in a fashion that can be understood qualitatively from scaling arguments. Semidilute chains overlap substantially so that large-scale properties (osmotic pressure, ...) are generally independent of the chain molecular weight.[93] The correlation length ξ describing the average interchain distance is still large in the semidilute regime in comparison with the Kuhn length l, but for concentrated solutions, ξ becomes the order of l and packing effects become important (see Appendix B). The cross-sectional area A of the polymer is a basic parameter controlling the local packing, and we can anticipate G_N and η_0 to depend strongly on A in concentrated polymer solutions. Application of the continuous chain model to the condensed regime is inappropriate because these model chains have no cross-sectional area. A physically acceptable theory of a condensed polymer fluid requires a more realistic model of flexible "strings" with a hard-core radius, but such a model would demand great mathematical sophistication. Qualitative aspects of condensed polymer systems can be understood by using scaling arguments to correct for the unphysical description of local interactions in the Gaussian chain theory.

The vague term entanglement seems to suggest that the effect has something to do with chains looping about each other as in a knotted string. Stiff chains, however, show the same characteristic entanglement effects[1,88] as flexible chains so that the looping picture is at best a secondary aspect of the entanglement interaction.

The presence of entanglement effects in rod solutions and the predominance of packing effects in concentrated solutions imply that we should seek to understand entanglement in terms of local orientational correlations between chains. For example, it is known from Flory's mean-field theory of rod polymers[94] that strong orientational correlations occur for a critical axial ratio of the rod length $\mathcal{L}$ to diameter $\mathcal{D}$. The Flory theory predicts a critical value of $x = \mathcal{L}/\mathcal{D}$ of roughly 7, which agrees qualitatively with experimental observations of a critical x, which equals about 5. (See ref 95.) The "break point" in the viscosity curve separating low molecular weight and high molecular regimes in the rod viscosity data of Baird and Ballmann[88] occurs for $x \sim O(10)$. Aharoni[95] tabulates values of x for several stiff polymers and observes a break point in intrinsic viscosity data for stiff polymers. These results suggest a connection between chain packing and entanglement.

There are many technical problems in the measurement and interpretation of the zero-shear viscosity of rod solutions, especially in polyelectrolyte solutions, so it is useful to consider a generalization of the Flory axial ratio to flexible uncharged polymers. It is natural to replace the rod length by the characteristic measure of flexible polymer size, the root-mean-square end-to-end distance $\langle R^2\rangle^{1/2}$. We then define the "axial ratio" by

$$x \equiv \langle R^2\rangle^{1/2}/\mathcal{D} \tag{3.19}$$

where $\mathcal{D}$ is the chain diameter. A recent correlation[96] of the entanglement molecular weight $M_e°$ (see Appendix B) in the melt with the chain cross-sectional area gave the universal relation

$$(\langle R^2\rangle_\theta/M)M_e°/A \approx 27 \tag{3.20}$$

where $\langle R^2\rangle_\theta$ is obtained from dilute-solution intrinsic viscosity measurements assuming Gaussian chain dynamics and the chain cross-sectional area A is obtained from crystallographic data. $(\langle R^2\rangle_\theta/M)M_e°$ is the end-to-end distance $\langle R^2\rangle$ of a chain having the entanglement molecular weight $M_e°$ so that (3.20) becomes

$$\langle R^2\rangle_e/A \approx 27 \tag{3.21}$$

Since the diameter $\mathcal{D}$ is related to the area A by $A = \pi(\mathcal{D}/2)^2$, we can rewrite (3.21) as

$$x(\text{entanglement}) \approx 5 \tag{3.22}$$

which is similar to the Flory estimate of x_c for rods. The ratio of $\langle R^2\rangle$ to its entanglement value $\langle R^2\rangle_e$

$$\langle R^2\rangle/\langle R^2\rangle_e = M/M_e° \tag{3.23}$$

provides a natural measure of entanglement coupling, which is independent of system-dependent parameters such as the chain cross-sectional area. In general, the entanglement molecular weight depends on concentration in the Flory theory of the packing of rods, and the concentration dependence of M/M_e is discussed below. $M_e°$ denotes M_e in the bulk.

The entanglement parameter β_F in (3.11b) has the limiting "unentangled" value

$$\beta_F(M \ll M_e) \approx 0 \tag{3.24a}$$

and empirically the "crossover point" from entangled to unentangled behavior of the viscosity occurs for a critical value of the molecular weight M_c on the order of M_e.[1,2] In the Bueche theory M_e and M_c are related by a factor of roughly 2, which is a reasonable empirical approximation.[1]

$$M_c \approx 2M_e \text{ (empirical)} \tag{3.25}$$

At high molecular weights β_F in (3.12a) approaches the limiting entangled value

$$\beta_F(M \gg M_e) \approx 2/(d+2) \equiv \beta_F^* \tag{3.24b}$$

An interpolatory function between the limits (3.24a) and (3.24b) is given by

$$\beta_F(M/M_e) \approx \beta_F^*(M/2M_e)/(1 + M/2M_e) \tag{3.26}$$

The flow modulus prefactor $G_F(t=0;M/M_e)$, which generalizes (3.12a), depends on M/M_e, and it is necessary to address this dependence if η_0 is to be described over a wide range of molecular weights and concentrations. A sum of Rouse and entangled chain contributions to $G_F(0)$ gives

$$G_F(0) \approx (cRT/M)[1 + M/M_e], \quad G_F(0,M/M_e \gg 1) = G_N \equiv cRT/M_e \tag{3.27}$$

which recovers the correct modulus in the unentangled and entangled regimes [see (3.13d) and 3.12a)]. Next, we consider the difficult problem of the concentration dependence of τ_F. We replace M in (3.13) by the dimensionless variable M/M_e.

$$\tau_R(c) \propto \tau_g^*(M/M_e)^{(d_f+2)/d_f}\, h(M_e) \tag{3.28}$$

where $h(M_e)$ is an *unspecified* function of concentration through M_e. The flow relaxation time τ_F generalizing (3.14b) becomes

$$\tau_F(c) \sim [(M/M_e)^{(d_f+2)/d_f}\, \tau_g^*]^{1/[1-\beta_F(M/M_e)]} g(M_e) \tag{3.29}$$

where $g(M_e)$ is related to the unknown function $h(M_e)$ in (3.28). Consistency requirements are employed to estimate $g(M_e)$ below. Plazek and Ngai[62,97] have examined time–temperature superposition data in the glassy transition and terminal relaxation regimes and find consistency with the temperature dependence of τ_F in (3.29) where $\beta_F \approx 2/5$.

The viscosity from (3.16) is given by $\eta_0 \sim G_F(0)\,\tau_F$, so that from (3.27) and (3.29) we have

$$\eta_0(c,M,T) \approx G_F(0)\, g(M_e)\, [(M/M_e)^{(d_f+2)/d_f}]^{1/[1-\beta_F(M/M_e)]} \times F(\tau_g{}^*,M/M_e) \quad (3.30a)$$

where the "friction factor" equals

$$F(\tau_g{}^*,M/M_e) \approx (\tau_g{}^*)^{1/[1-\beta_F(M/M_e)]}, \quad F(\tau_g{}^*,M \gg M_e) \equiv F(\tau_g{}^*) \quad (3.30b)$$

The unspecified function of concentration $g(M_e)$ in (3.30a) can be estimated from the physical condition that η_0 is independent of M_e for unentangled polymer solutions. This consistency requirement is satisfied by taking $g(M_e)$ to scale as

$$g(M_e) \sim M_e{}^{(d_f+2)/d_f} \quad (3.30c)$$

Equation 3.30a with $g(M_e)$ specified by (3.30c) simplifies in the limits of highly entangled ($M \gg M_e$) and unentangled ($M \ll M_e$) flexible ($d_f = 2$) chains

$$\eta_0 \sim G_N M_e{}^2 (M/M_e)^{2(d+2)/d} (\tau_g{}^*)^{(d+2)/d}, \quad M > M_c \quad (3.30d)$$

$$\eta_0 \sim (cM) RT \tau_g{}^*, \quad M < M_c \quad (3.30e)$$

For entangled concentrated solutions of flexible polymers, we obtain the concentration dependence

$$\eta_0/F(\tau_g{}^*) \sim (cM)^{10/3}, \quad \tau_F/F(\tau_g{}^*) \equiv \hat{\tau}_F \sim M^{10/3} c^{4/3}, \quad G_N \sim c^2, \quad M_e \sim c^{-1} \quad (3.30f)$$

The concentration dependencies of G_N and M_e become more complicated in semidilute swollen ($d_f \approx {}^5/_3$) entangled polymer solutions (see Appendix B). From (B.8), (3.29), and (3.30a) we obtain ($M \gg M_e$)

$$\eta_0/F(\tau_g{}^*) \sim c^{49/12} M^{11/3}, \quad \hat{\tau}_F \sim c^{11/16} M^{11/3}, \quad G_N \sim c^{9/4}, \quad M_e \sim c^{-5/4} \quad (3.30g)$$

The experimental concentration and molecular weight dependence of the normalized viscosity, $\eta_0/F(\tau_g{}^*,M/M_e) \equiv \eta$, of concentrated polymer solutions are investigated by Berry and Fox,[99] who obtain the correlations

$$\hat{\eta} \sim (cM)^{3.4}, \quad M > M_c \quad (3.30h)$$

$$\hat{\eta} \sim cM, \quad M \le M_c \quad (3.30i)$$

A more recent systematic study of moderately concentrated solutions of polystyrene in good solvents by Hager and Berry[98] indicates

$$\hat{\eta} \sim (cM)^{\alpha}, \quad 3.5 \le \alpha \le 4.0 \text{ or } \hat{\eta} \sim c^4 M^{3.4}, \quad M > M_c \quad (3.30j)$$

$$\hat{\eta} \sim cM, \quad M \le M_c \quad (3.30k)$$

The dependence of $\hat{\eta}$ on concentration and molecular weight is in accord with (3.30f) for concentrated polymer solutions. There seems to be some support for a larger concentration and molecular weight dependence in good solvents as predicted by (3.30g). The evidence is firm for a concentration exponent close to 4 in moderately concentrated good solvent polymer solutions,[99] but the evidence for a larger viscosity molecular weight exponent is weak. Further studies are needed to check the predictions of (3.30g). In the next section we discuss the related problem of the solvent dependence of the diffusion coefficient molecular weight exponent.

E. Diffusion Coefficient. Other transport properties can be obtained in a fashion similar to the zero-shear viscosity. The diffusion coefficient D reflects a many-chain diffusion process and should correspond to the average time for a group of correlated chains to move a distance on the order of the polymer dimensions $\langle R^2 \rangle^{1/2}$. The relaxation time for diffusion should then be related directly to the flow relaxation time, τ_F.

From dimensional analysis the diffusion coefficient D scales as

$$D \sim L^2/\tau_F \quad (3.31)$$

and in a concentrated polymer solution the relevant polymer dimension L is $\langle R^2 \rangle^{1/2}$. From (3.29) and (3.30c) we then have

$$D \sim (\tau_g{}^*)^{-1/[1-\beta_F(M/M_e)]} \langle R^2 \rangle [(M/M_e)^{-(d_f+2)/d_f}]^{1/[1-\beta_F(M/M_e)]} M_e{}^{-(d_f+2)/d_f} \quad (3.32)$$

For high molecular weights, where the glass transition temperature T_g is independent of M and where $\beta_F \rightarrow \beta_F{}^* = 2/(d + 2)$, the diffusion coefficient for a concentrated flexible ($d_f = 2$) polymer solution scales as

$$D \sim (1/M)(M/M_e)^{-4/d}, \quad M > M_c; \quad D \sim 1/M, \quad M < M_c, \ d_f = 2 \quad (3.33a)$$

where the friction coefficient term $F(\tau_g{}^*, M/M_e)$ is omitted. At high dimensions ($d \rightarrow \infty$) we recover the Rouse theory result[17]

$$D \sim M^{-1} \quad (3.33b)$$

and in three dimensions with flexible chains ($d_f = 2$) we obtain ($M_e \sim c^{-1}$)

$$D(d=3) \sim (1/M)(cM)^{-4/3}, \quad M > M_c; \quad D \sim M^{-1}, \quad M < M_c \quad (3.33c)$$

From (3.14d) and (3.31) the molecular weight dependence of D for swollen semidilute entangled chains,[86] $d_f \approx (d + 2)/3$, becomes

$$D \sim M_e{}^{(2/d)(d+8)/(d+2)} M^{6/(d+2)-(8+d)/d}, \quad M > M_c, \quad 2 < d \le 4 \quad (3.33d)$$

$$D(d=3) \sim c^{-11/6} M^{-37/15}, M > M_c, \quad M_e \sim c^{-5/4}, \quad d = 3$$

As in the case of the viscosity, the molecular weight dependence of the diffusion coefficient reduces to the reptation theory prediction in four dimensions[3,4]

$$D \sim M^{-2}, \quad M > M_c, \quad d = 4 \quad (3.33e)$$

The reptation model prediction for the diffusion coefficient of entangled polymers $D \sim M^{-2}$ has stimulated many recent experimental studies. Watanabe and Kotaka[100] compiled polystyrene melt data obtained by five groups, and Nemoto et al.[101] review data for concentrated and semidilute entangled polystyrene/dibutyl phthalate solutions. In general, the data obtained by the different groups are remarkably consistent although there is not complete agreement on the molecular weight exponent obtained from their data analyses. Watanabe and Kotaka[100] found a reasonable fit to the polystyrene melt data assuming the reptation model exponent −2. However, no confidence interval was estimated for the exponent, and a best fit of the data was apparently not attempted. A simple graphical estimate of the polystyrene melt data led us to a best fit value of -2.2 ± 0.1 so that we would like to see a careful estimate of the diffusion coefficient exponent and the confidence interval. For concentrated (40%) and semidilute entangled solutions of polystyrene, the diffusion coefficient exponent is quite definitely larger than the reptation model estimate. Nemoto et al.[101] report the diffusion coefficient exponent of -2.6 ± 0.2 and a corresponding viscosity exponent of 3.5 ± 0.1 for polystyrene/dibutyl phthalate solutions. The melt data are reasonably consistent with the diffusion coefficient estimate $^{-7}/_{3} \approx -2.33$ from (3.33c), and the concentrated/semidilute solution results of Nemoto et al. are consistent with the swollen chain predictions in (3.17c) and (3.33d), which indicate a diffusion coefficient exponent $^{-37}/_{15} \approx -2.47$ and the viscosity exponent $^{11}/_{3} \approx 3.67$. The concentration dependence of tracer diffusion data by Nemoto et al.[101] indicates a power law dependence with exponent -1.5, which is in the range predicted by (3.33c) and (3.33d) (see Appendix B).

The simulation of polymer melts by computer has developed to the point that chains of reasonable length and number can be simulated. Kremer et al.[102] note that the diffusion coefficient molecular weight exponent obtained in their simulations is lower than the expected value -2, and they conjecture that crossover effects are responsible for the deviation. Very recently Deutsch and Madden[103,104] provided simulation estimates of the viscosity and diffusion coefficient molecular weight exponents along with confidence intervals

$$\eta_0 \sim M^{3.41 \pm 0.14} \tag{3.34a}$$

$$D \sim M^{-2.50 \pm 0.04} \tag{3.34b}$$

which are consistent with (3.14), (3.17c), and (3.33d).

F. Branched Polymers. The properties of polymeric fluids can be significantly modified through a variation of molecular architecture because of two basic influences of branching: (1) Branching changes the average local polymer density relative to a linear chain.[105] (2) Motion of the chain is restricted by junctions. A junction can move only by concerted motion of the different parts (arms in a star polymer) of the molecule. A review of dilute-solution static and dynamic properties of branched polymers is given by Douglas et al.[106]

The previous section was confined to linear polymers since branching introduces significant new features into the description of concentrated polymer solution dynamics. We schematically illustrate the application of our semiempirical relaxation model to polymer ring and uniform star polymer fluids.

Ring polymers provide an interesting test of the effect of topological constraints on polymer melt properties. The Rouse theory[1,2,17] leads us to expect that the viscosity of relatively small rings should be about half that of linear chains of the same molecular weight since the ratio of the radii of gyration $\langle S^2\rangle(\text{ring})/\langle S^2\rangle(\text{linear})$ equals $^1/_2$ for Gaussian chains. As usual the Rouse theory holds fairly well for melts of relatively short chains and the predicted ratio of melt viscosities of about $^1/_2$ is observed.[107] For longer rings we expect the viscosity and diffusion coefficient to have roughly the same molecular weight, concentration, and temperature dependence as linear chains. From (3.21), however, we expect a change in the entanglement molecular weight $M_c°$. Taking the radius of gyration as the appropriate measure of polymer size in (3.21) yields

$$M_e°(\text{ring})/M_e°(\text{linear}) \approx M_c°(\text{ring})/M_c°(\text{linear}) \approx 2 \tag{3.35}$$

which is close to the estimate of 1.8 by McKenna et al.[107] The experimental data are too limited to establish whether or not this is a definitive result, but the agreement is encouraging.

Recent theory and simulation data suggest that ring polymers swell in the presence of linear chains.[108] Apparently the presence of toplogical constraints can upset the delicate balance of forces which causes linear chains to adopt a nearly Gaussian chain configuration in concentrated polymer solutions. Experimentally the viscosity of a melt of polymer rings increases greatly with the addition of a small amount of linear material.[107,109] Our relaxation model suggests these phenomena are related. Equation 3.30a implies that chain swelling increases the viscosity molecular weight exponent (see ref 99). Specifically, if we assume that sufficient linear material has been added to swell the rings to good solvent dimensions in dilute solution, then we have $\eta_0(\text{ring/linear}) \sim M^{11/3}$. This increase in the molecular weight exponent is consistent qualitatively with the observed large enhancement of the ring melt viscosity with the addition of linear chains.[107,109] It would be interesting to measure the radius of gyration of the rings in the melt to see if it is increasing with dilution by linear chains.

A star polymer is the simplest branched polymer species that illustrates the role of junction points on the center of mass diffusion of the polymer. Movement of the star junction requires the cooperative motion of the star arms, and we anticipate that the relaxation time for the center of mass motion of the junction should be larger than that for a linear chain when the chain arms are long. For stars with short arms the Rouse theory[1,2] indicates that stars have a smaller relaxation time (viscosity) than linear polymers, as in the ring example discussed above. For long entangled star arms, however, a simple transition state model with a potential barrier height E_{arm} proportional to the star arm length M_{A} provides a reasonable model for calculating the flow relaxation time, and we estimate

$$\tau_{\text{F}}(\text{star}) \sim \exp(E_{\text{arm}}/k_{\text{B}}T) \tag{3.36a}$$

$$E_{\text{arm}} = \gamma(M_{\text{arm}}/M_e) \tag{3.36b}$$

where γ is a nonuniversal constant. From (3.16), (3.31), and (3.36) we then expect $\eta_0(\text{star})$ and $D(\text{star})$ to have the dominant scaling behavior

$$\eta_0(\text{star}) \sim \exp(\gamma M/M_e), \quad D \sim \exp(-\gamma M/M_e) \tag{3.36c}$$

Experimental evidence supports a dominant exponential rather than the power law dependence of the melt viscosity and diffusion coefficient of stars with long arms ($M > M_e$).[110] Helfand and Pearson[111] develop a rather successful model, leading to the scaling behavior (3.36c), which is phrased in terms of the reptation model. However, the notion of a branch length dependent barrier potential transcends the particular modeling of molecular motion in terms of reptation.

4. Conclusions

Relaxation in condensed materials is usually described in terms of idealized molecular models (defect diffusion,[46] reptation in polymers,[3,4] ...) or in terms of purely phenomenological correlations (power law,[22,47] stretched exponential relaxation functions,[21,46] Vogel temperature dependence of the zero-shear viscosity and diffusion coefficient,[1,17] ...). The formulation of a molecular relaxation model represents only a guess of the relaxation mechanism. Purely phenomenological correlations are useful for concisely summarizing data and for stimulating new theories when regularities are found, but they do not provide a detailed understanding of the molecular processes underlying the observed correlations.

Relaxation in polymeric materials, and condensed materials in general, exhibits striking regularities,[1,21,25] which are apparently insensitive to many of the details of molecular interaction and the type of perturbation. Deviations from the simple exponential decay of classical relaxation models are commonly observed, but phenomenological relaxation functions are generally found to belong to a small class of functions.[21,25] Time–temperature superposition is often exhibited over a significant range of time and temperature (see Appendix A). Relaxation times often have the characteristic Vogel form,[1,17] and relaxation functions are often characterized by "critical indices", which are reminiscent of critical phenomena. These universal correlations suggest that something very interesting is behind the observed regularities—perhaps a statistical law that is insensitive to the details of molecular interaction.

We have formulated a semiempirical approach to relaxation in condensed materials, which provides a middle ground between the detailed, but somewhat artificial, molecular models and the purely phenomenological correlation approach. This abstract formulation leads to a succinct description of memory effects that are responsible for nonexponential relaxation in condensed materials. In this formalism we absorb all our ignorance about the details of the relaxation process into the memory kernel. Of course, there is little hope of an exact calculation of the memory kernel for systems of physical interest, but relaxation functions are readily measured and reasonable models of the memory kernel can be developed based on simple physical arguments. This is the crux of our semiempirical approach to condensed matter relaxation.[6]

The general integral equation formulation of relaxation in disordered condensed materials is applied to polymer melt viscoelasticity. This application requires the introduction of a specific model of the inhomogeneity in the structure of a polymer melt and a general conception of the physical processes responsible for glassy and terminal relaxation. A classical model of the origin of fluid viscoelasticity by Maxwell[12] and Gemant[13] is taken to be an appropriate starting point; however, we *strictly avoid* assuming that the condensed material is homogeneous. The assumption of a mean-field average molecular environment in a condensed material is not generally a good idea in the description of dynamics. This principle is well-known in modeling the electronic properties of disordered materials.[84]

The modeling of relaxation in section 3 emphasizes the estimation of the disorder parameter β. The ϕ parameter, which is interpreted as a measure of cooperativity of local motion, is expected to gain in importance upon going to the solid state.[6] Observe that the model relaxation function $\Psi(t;\beta;\phi)$ in (2.11) changes from stretched exponential to power law decay for $\phi \neq 1$. The integral of $\Psi(t;\beta,\phi)$ for $\phi \in (0,1)$ *diverges*, which is consistent with a solidlike response (infinite viscosity when $\Psi(t;\beta,\phi)$ corresponds to stress relaxation; see section 3B). It should be possible to monitor a transition between stretched exponential "liquid" relaxation to power law "solid" relaxation by cross-linking a polymer melt and observing the change in the terminal relaxation regime as a function of cross-linking. Chaset and Thirion[112] observed an approximate power law relaxation from the rubbery plateau upon cross-linking of a polymer melt, an observation which accords with the general expectation of our relaxation model. A model of ϕ for cross-linked polymer solutions should allow us to predict time–cross-linking superposition[112,113] of the terminal relaxation of polymer networks through (2.10e). Perhaps a simple model of the variation of ϕ will allow us to understand the transition between the liquid and solid states in amorphous materials.

Acknowledgment. We thank Greg McKenna for useful discussions.

Appendix A

Dilation Symmetry of the Memory Kernel and Time–Temperature Superposition. It is commonly observed that relaxation functions and frequency-dependent susceptibilities in complex materials are independent of temperature, pressure, and other parameters, aside from a rescaling of time or frequency (see Leaderman,[33] Ferry,[1] and Shore and Zwanzig[114]). We show that the implication of this rather general observation is that the memory kernel has a kind of symmetry. This observation alone can be used to motivate the introduction of the model memory kernel (2.7b).

Consider the integral equation (2.3a) for the relaxation function $\Psi(t)$ in the linear response approximation and rescale the time coordinate as $T = t/s$. Introducing the new variable into (2.3a) gives

$$\frac{\mathrm{d}\Psi(T)}{\mathrm{d}T} = -s^2\int_0^T \Omega_0 k_\delta(Ts,T's)\Psi(T')\mathrm{d}T' \tag{A.1}$$

where the coupling parameter Ω_0 has been added [see (2.7b)]. Observe that the δ function memory kernel, $k_\delta(t-\tau') = \Omega_0\delta(T-\tau')$, has a dilation symmetry

$$k_\delta = \Omega_0\delta(t-\tau') = \Omega_0\delta(Ts-T's) = (\Omega_0/s)\,\delta(T-T') \tag{A.2}$$

so that (A.1) becomes

$$\frac{\mathrm{d}\Psi(T)}{\mathrm{d}T} = -(\Omega_0 s)\int_0^T k_\delta(T-T')\,\Psi(T')\mathrm{d}T' \tag{A.3}$$

which is the same integral equation as (A.1) except for a new time coordinate and a rescaled coupling parameter $\Omega_0 \to \Omega_0 s$. In physical systems the coupling parameter Ω_0 is a function of temperature, pressure, concentration, etc. We then see that by rescaling the time coordinate a universal master curve for varying temperature, ..., etc., can be obtained provided the memory kernel has dilation symmetry as

$$K(Ts,T's) = s^\gamma K(T,T') \tag{A.4}$$

where γ is a constant. The observance of time–temperature superposition in physical systems indicates that the memory kernel at least approximately has this scaling symmetry.

The class of deterministic functions that have the dilation symmetry (A.4) is limited. This class includes the δ function and its derivatives and nondifferentiable "fractal" functions such as the Weierstrass function.[115] Power law functions correspond to the simplest general class of homogeneous functions. The model memory kernel (2.7b), for example, has the scaling property

$$K(ts,\tau s;\phi,\beta) = s^{\phi-2-\beta}K(t,\tau;\phi,\beta) \qquad \text{(A.5)}$$

Appendix B

Scaling Argument for the Concentration Dependence of the Plateau Modulus. In the Gaylord–Douglas[116] model of rubber elasticity the shear modulus of a rubber in the limit of low cross-linking density, $\bar{\nu}$, is dominated by a nonclassical contribution G_e, which derives from the network chains being "localized" by surrounding chains. The primary influence of this localization effect is to reduce the average degrees of freedom of the polymer so that there is an extensive change in the free-energy relative to a chain that is not localized. The change in the free-energy of a network chain from localization scales as[116]

$$\Delta F(\text{localization})/k_BT \sim n \sim \langle R^2\rangle_0/\xi^2 \qquad \text{(B.1)}$$

where n is the average number of segments in a network chain. (B.1) is implied generally by the Feynman–Kac theorem (see Douglas),[117] and this limiting behavior is sometimes referred to as "ground-state dominance". At high densities the mean-square end-to-end distance of a network chain scales as $\langle R^2\rangle_0 \sim n$, and the scale ξ, required by dimensional analysis, characterizes the scale of localization of the chain in the condensed state. The confinement contribution G_e° to the shear modulus of a rubber is proportional[116] to ΔF(localization) in (B.1) times $\bar{\nu}$, and $\bar{\nu}\langle R^2\rangle_0$ is proportional to the polymer density, ρ.

The polymer molecules in an incompressible polymeric material occupy a finite fraction of the sample volume so that the lateral confinement radius ξ should be on the order of the hard-core radius of the polymer chain. If we consider the entire macroscopic sample as one giant molecule whose volume is on the order of the macroscopic volume, then we obtain a relation between ξ and the polymer density[116]

$$\xi_o \sim \rho^{-1/(d-1)} \qquad \text{(B.2a)}$$

where the degree subscript or superscript indicates the bulk state. Further, upon dilution we obtain

$$\xi \sim \xi_o\phi^{-1/(d-1)}, \quad c = \rho\phi \qquad \text{(B.2b)}$$

where ϕ is the polymer volume fraction. From (B.1) and (B.2a) the "localization modulus" G_e upon dilution becomes

$$G_e^\circ \sim \bar{\nu}\langle R^2\rangle_0/\xi^2 \rightarrow G_e \sim G_e^\circ\phi^{(d+1)/(d-1)} \qquad \text{(B.3)}$$

in the high concentration limit. A critical concentration $c^{**} \sim M/L\xi_o^{d-2}$, where $L\xi_o^{d-2}$ is on the order of the hard-core molecular volume with L the chain length, determines the onset of the concentrated regime where the polymers occupy a significant fraction of the available volume. Since the chain length L is proportional to M, the critical concentration c^{**} is independent of molecular weight and inversely related to the chain monomer dimensions. Experimental estimates[118] of the onset of the concentrated regime place c^{**} on the order 0.1 g/mL. The packing argument[116] for G_e° also implies a rough inverse proportionality of G_e to the chain cross-sectional area A, i.e., $\xi_o^2 \sim O(A)$. Ferry[1] notes that the plateau modulus decreases with increasing side-group length in qualitative support of the inverse relationship between G_e and A. Miller and Boyer[119] find an inverse relationship between $M_e^\circ \sim 1/G_N^\circ$ and the chain cross-sectional area A. Further studies would be useful.

Experimental data by McKenna et al.[120] confirms the Gaylord–Douglas model prediction[116] that G_e° approximately equals the plateau modulus G_N° in the limit of low cross-linking (cross-linking sufficiently high that an equilibrium modulus exists). The degree superscript denotes the undiluted polymer property. The identification[107] $G_e^\circ \approx G_N^\circ$ and (B.3) imply

$$G_N \sim G_N^\circ\phi^{(d+1)/(d-1)}, \quad G_N \equiv cRT/M_e \qquad \text{(B.4)}$$

which is equal to (3.12c).

Equation B.4 becomes modified if the chains swell significantly, $\xi^2 \gg A$, while remaining entangled. The semidilute regime is hypothetically divided into entangled and unentangled regimes. Experiment[118] indicates that for small-molecule solvents the critical entanglement concentration c_e is about 5–10c^* where c^* is the usual coil overlap concentration, $c^* \sim M/\langle R^2\rangle^{d/2}$. Thus, $c^* < c < c_e$ defines the unentangled semidilute regime, and the range $c_e < c < c^{**}$ defines the entangled semidilute regime. The critical concentration c_e is expected to depend rather sensitively on the solvent. Polymer clustering and thus "entanglement-like" response should be favored in poor solvents so that c_e should be lower in poor solvents. This is in accord with experimental observations.[118]

In the entangled semidilute regime the chains can swell so that we replace[118] (B.1) by

$$\Delta F(\text{localization}) = \langle R^2\rangle^{d_f/2}/\xi^{d_f}, \quad \langle R^2\rangle \sim M^{2/d_f}, \quad c > c_e \qquad \text{(B.5)}$$

where d_f is the chain fractal dimension, $\langle R^2\rangle \sim M^{2/d_f}$. From standard scaling arguments the static correlation length, ξ, in the semidilute regime scales as[93]

$$\xi \sim \langle R^2\rangle^{1/2}(c/c^*)^{-1/(d-d_f)}, \quad c_e < c < c^{**} \qquad \text{(B.6)}$$

so that G_e becomes

$$G_e \sim \phi\Delta F(\text{localization}) \sim \phi^{d/(d-d_f)} \sim \xi^{-d}, \quad c_e < c < c^{**} \qquad \text{(B.7)}$$

We then infer the concentration dependence of the plateau modulus in the semidilute entangled regime as

$$G_N \sim \phi^{d/(d-d_f)}, \quad G_N = cRT/M_e, \quad c_e < c < c^{**} \qquad \text{(B.8)}$$

(B.8) reduces to Doi's prediction,[120] $G_N \sim \phi^3$, for Gaussian chains ($d_f = 2$, $d = 3$) and to de Gennes' scaling prediction,[93] $G_N \sim \phi^{9/4}$, for swollen chains ($d_f \approx {}^5/_3$, $d = 3$). We could not understand de Gennes' c^* theorem derivation[93] of the concentration scaling of G_N in (B.8), so it is hoped that (B.5)–(B.8) provide some clarification. See Freed[122] for an elaboration of the scaling approach to entangled polymer dynamics.

The concentration dependence of η_0 and D in entangled semidilute poor solvents ($d_F = 2$) is different from that predicted by (3.30f) and (3.33c) for the concentrated regime. We expect T_g and hence the friction function $F(\tau_g{}^*)$ to be relatively insensitive to variations in concentration at such relatively low concentrations. The scaling of M_e with concentration is also changed according to (B.8). Inserting (B.8) in (3.30d) and (3.32) and taking $d_f = 2$ and $d = 3$ imply

$$\eta_0 \sim c^{17/3}M^{10/3}, \quad \hat{\tau}_F \sim c^{8/3}M^{10/3}, \quad D \sim c^{-8/3}M^{-7/3}, \quad c_e < c < c^{**}, \quad M > M_e \qquad \text{(B.9)}$$

where $F(\tau_g{}^*)$ is neglected (see below) in (B.9).

Data in the semidilute entangled regime are more limited than data obtained in the concentrated regime. Wheeler and Lodge[123] obtained tracer diffusion data for polystyrene in poly(vinyl methyl ether) in the semidilute entangled regime, which indicates $D \sim M^{-2.3\pm0.2}c^{-3.3}$, and Noda et al.[118b] obtain zero-shear viscosity data in entangled semidilute solutions of poly(α-methylstyrene) in Θ solvents, which gives $\eta_0 \sim c^{6.8}M^{3.4}$. Adam and Delsanti[124] provide extensive data for semidilute solutions of polystyrene in the Θ solvent cyclohexane: $\eta_0 \sim c^{5.14\pm0.16}M^{3.37\pm0.05}$, $\tau_F \sim c^{2.8\pm0.05}M^{3.75\pm0.05}$, $G_N \sim c^{2.5\pm0.2}$. The stronger concentration dependence of τ_F in a Θ solvent is notable. These observations accord qualitatively with (B.9), but further experimental studies of the semidilute entangled regime seem warranted.

The apparent concentration dependence of transport properties in concentrated solutions ($c \geq c^{**}$) is greatly affected by the treatment of the friction function $F(\tau_g{}^*)$. The glass transition temperature depends on concentration, and thus $F(\tau_g{}^*)$ can exhibit a very strong concentration dependence for $c > c^{**}$. Experimentally[125] $F(\tau_g{}^*)$ seems to mimic a power law dependence on concentration over an appreciable range, $F(\tau_g{}^*) \approx c^{1.6}$, so that the viscosity in (3.30f) scales with concentration to roughly the fifth power [see also (B.9)] when η_0 is not reduced by $F(\tau_g{}^*)$ according to the methods of Berry and Fox.[99] An apparent fifth power concentration dependence of η_0 is often observed.[1,125] Similarly, the concentration dependence of $F(\tau_g{}^*) \sim c^{1.6}$ affects the concentration dependence of D, which without "normalization" yields an approximately $c^{-3}[F(\tau_g{}^*) \approx c^{1.6}]$ dependence on concentration instead of the $c^{-4/3}$ estimate in (3.33c). Thus, we obtain some understanding of how Nemoto et al.[101] could obtain a $c^{-1.5}$ concentration dependence for the reduced diffusion coefficient $D/F(\tau_g{}^*)$ while Kim et al.[126] obtain an approximately c^{-3} dependence for the *same data* reduced to the diffusion coefficient at a dilute-solution concentration. The apparent concentration dependences of concentrated polymer solution transport properties are evidently sensitive to the method of data reduction.

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