Nonexponential density relaxation and the dynamic form-factor of polymer melts in the reptation regime

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A microscopic theory is developed for relaxation of the composition of high-polymer melts. A method due to I. M. Lifshitz is used to derive explicit expressions for the kinetic coefficients and generalized susceptibilities in terms of the corresponding parameters for a broken bond system and the dynamic characteristics of the individual macromolecules (the latter are explicitly calculated using the Doi-Edwards model). The nonexponential relaxation which is specific to high-polymer melts (as opposed to low-molecular mixtures) is caused by the frequency dispersion of the kinetic coefficients and is analyzed in detail. Various limiting expressions for the dynamic form-factors are also considered.

1. INTRODUCTION

Polymer mixtures and melts occupy a unique place in condensed-state physics because they can be regarded as model systems in which the critical phenomena are "frozen-in." Indeed, because the polymers consist of macromolecules, two characteristic space-time scales can be distinguished. Rearrangement processes involving only a few polmer units or small molecules present in the system occur during a characteristic time t_0 over a characteristic distance r_0. Although the specific mechanism responsible for the rearrangement may differ from the corresponding restructuring ("elementary jump" process) in low-molecular liquids, it is clear that the characteristic scales in both cases are of the same order of magnitude. They are therefore small compared to the characteristic scales T_M and R_M for global rearrangements of the individual macromolecules (equivalently, the characteristic space-time correlation scales for bond density fluctuations in the macromolecules):

$$T_M \gg t_0, \quad R_M \gg r_0. \tag{1.1}$$

These inequalities, which are specific to polymers, give rise to similar inequalities

$$t_c \gg t_0, \quad r_c \gg r_0 \tag{1.2}$$

for the scales t_c and r_c characterizing the collective fluctuation-dissipation behavior. For $t \gg t_0$ and $r \gg r_0$, this behavior is dominated by the simple fact that the monomer units are linked ("linear memory" in the terminology of I. M. Lifshitz[1]) and is therefore quite general. On the other hand, it is also by no means simple to analyze, because inequalities (1.2) imply that even for these times and distances, the kinetic coefficients that govern the diffusion relaxation of the system should be subject to considerable spatial and temporal dispersion.[2] The purpose of the present paper is to develop a systematic macroscopic relaxation theory for a general multicomponent polymer system with n different kinds of bonds. We will use the theory to analyze some characteristic features of the fluctuation-dissipation behavior of high-polymer systems for the case of binary polymer melts.

As usual,[3,4] such a theory reduces to calculating the generalized susceptibility matrix $\alpha(\mathbf{q},p)$ for the response of the system to an external field $\varepsilon_i(r,t)$ applied to bonds of type i:

$$-\Delta_i(\mathbf{r},t) = \int_0^\infty d\tau \int dV' \alpha_{ij}(\tau, \mathbf{r}-\mathbf{r}')\,\varepsilon_j(\mathbf{r}', t-\tau), \tag{1.3}$$

$$\alpha_{ij}(\mathbf{q},p) = \int_0^\infty dt \int dV \alpha_{ij}(t,\mathbf{r}) \exp(i\mathbf{qr}-pt). \tag{1.4}$$

Here $\Delta_i(\mathbf{r},t) = \rho_i(\mathbf{r},t) - \bar{\rho}_i$, where $\rho_i(\mathbf{r},t)$ is the density of the bonds of type i at point r and time t, and $\bar{\rho}_i$ is the corresponding average value for a system in thermodynamic equilibrium. According to the fluctuation-dissipation theorem, the matrix $\alpha(\mathbf{q},p)$ is related to

$$S_{kl}(\mathbf{q},t) = \int dV \langle \Delta_k(0,0)\Delta_l(\mathbf{r},t)\rangle \exp(i\mathbf{qr}), \tag{1.5}$$

the time-correlation function matrix of the bond densities; this relation can conveniently be expressed in the form

$$T\alpha(\mathbf{q},p) = \mathbf{G}(\mathbf{q}) - p\mathbf{S}(\mathbf{q},p), \tag{1.6}$$

where

$$\mathbf{S}(\mathbf{q},p) = \int_0^\infty dt \mathbf{S}(\mathbf{q},t) \exp(-pt)$$

and the elements of the matrix $\mathbf{G}(\mathbf{q}) = \mathbf{S}(\mathbf{q};t=0)$ are the static correlation functions of the densities of the structural units (bonds) in the polymer. (Here and below, functions in the $(\mathbf{r},t)$-and $(\mathbf{q},p)$-representations will be distinguished only by the choice of the letters used to denote their arguments; the summations convention will also be in force for repeated indices, so that $a_i b_i$ denotes a sum over i from 1 to n).

Equation (1.3) is equivalent to the relaxation equation

$$\frac{\partial}{\partial t}\Delta_i(\mathbf{q},t) = -q^2 \int_0^\infty d\tau \Lambda_{ij}(\mathbf{q},\tau)\,[\delta\mu_j(\mathbf{q},t-\tau) + \varepsilon_j(\mathbf{q},t-\tau)/T, \tag{1.7}$$

where in the linear theory the thermodynamic forces $\delta\mu_j(\mathbf{q},t)$ can be expressed as

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$$\delta\mu_i(\mathbf{q},\ t)=T(\mathbf{G}^{-1}(\mathbf{q}))_{ij}\Delta_j(\mathbf{q},\ t) \tag{1.8}$$

in terms of the conjugate density fluctuations $\Delta_i(\mathbf{q},t)$ and the matrix $\boldsymbol{\alpha}(\mathbf{q},p)$ is related to $G(q)$ and the kinetic coefficient matrix $\Lambda(\mathbf{q},p)$ by

$$\alpha^{-1}(\mathbf{q},p)=T[\mathbf{G}^{-1}(\mathbf{q})+(p/q^2)\boldsymbol{\Lambda}^{-1}(\mathbf{q},p)]. \tag{1.9}$$

It seems hopeless to attempt to calculate the generalized susceptibility directly for a system with a specified linear memory and volume interaction (by volume interaction, we mean the interaction that remains after all the polymer bonds have been broken). However, considerable progress can be made if we adopt the following formulation, which exploits the inequalities (1.1) and was first proposed by Lifshits.[1] In this approach, one assumes that the properties are already known for a system of small molecules which models the volume interaction for the polymer (regarded as a broken-bond system); the problem is then to find how the polymer differs from the model system when the linear memory is specified. (Volume interaction and broken-bond system are reviewed in Ref. 5.)

We use the Lifshitz approach in Sec. 2 to derive expressions relating the collective behavior of a polymer system to the corresponding behavior for a broken-bond system and to the structural properties that describe the behavior of individual molecules with a specified structure. This approach yields the dispersion of the kinetic coefficients automatically, which is an advantage over the methods employed in Refs. 6–8, where arbitrary assumptions had to be imposed on the form of the dynamic form-factor of the polymer melts. In particular, the frequency dispersion of the kinetic coefficients was not considered, even though it is responsible for linear memory in polymer melts. We analyze the frequency dispersion in Sec. 3 for the reptation regime,[9] which corresponds to the limiting case of strong topological interaction.[10,11] In Sec. 4 we derive expressions for the dynamic form-factor of polymer melts of various structure, and the (generally nonexponential) time relaxation for the diffusion modes of these systems is analyzed in Sec. 5. In addition to correcting and refining several results derived in Refs. 6–8 for mixtures of homopolymers A_N and B_N, we also succeed in analyzing for the first time the behavior of melts composed of block copolymers A_NB_M. (Because in block copolymers the thermodynamically incompatible units A_N and B_M are joined by an A–B chemical bond, the usual separation into two macroscopic phases is not observed—instead, a superstructure of period d forms where d is large compared to the interatomic distance r_0, and this accounts for the increased interest in these systems.[12–14]) Finally, in Sec. 6 we consider possible experimental confirmation of our results and explore what happens if the system has a small (but finite) compressibility, or if traces of highly mobile low-molecular impurities are present.

2. THE LIFSHITZ METHOD AND THE MOLECULAR FIELD APPROXIMATION IN THE MICROSCOPIC THEORY OF LINEAR RELAXATION FOR POLYMERS

We take the collective response (1.3) of the polymer material to an external field to be the sum of the responses of the individual macromolecules:

$$\Delta_i(\mathbf{r},t)=\sum\Delta_i^{(M)}(\mathbf{r},t;\{\varepsilon_M(\Gamma)\}), \tag{2.1}$$

where the summation is over all the macromolecules in the system. The form of (2.1) indicates that the mean partial contribution $\Delta_i^{(M)}$ from macromolecule M is a functional that depends on an effective field $\varepsilon_M(\Gamma)$, where Γ is a point in the configuration space of M. In general, ε_M depends on the structure of M and is not equal to the sum of the external fields acting on the structural units of M. This is because the external fields drive the systems away from thermodynamic equilibrium, so that the average interaction energy among the linked monomers in the macromolecule and between them and the rest of the system changes accordingly. However, it seems reasonable to suppose that the contribution of the intramolecular interaction to the effective field ε_M can be neglected to a first approximation. We then have

$$\varepsilon_M=\sum\tilde{\varepsilon}_j(\mathbf{r}_{\alpha_j},t)=\sum[\varepsilon_j(\mathbf{r}_{\alpha_j},t)+\varepsilon_j^*(\mathbf{r}_{\alpha_j},t)], \tag{2.2}$$

where the sum includes all the linked monomer units in the macromolecule M, and the molecular field $\varepsilon_j^*(\mathbf{r}_{\alpha j},t)$ is obtained by suitably averaging the volume interaction between the αth monomer unit of type j and all the other monomer units belonging to other macromolecules $M'\neq M$. Since this averaging is carried out over times $t\sim t_0$ and distances $r\sim r_0$ comparable to the "low-molecular" characteristic scales, the result should be insensitive to the polymer structure of the material and in our linear theory can be expressed in the form

$$\varepsilon_i^*(\mathbf{q},t)=T\int_0^\infty d\tau d_{ij}(\mathbf{q},\tau)\Delta_j(\mathbf{q},t-\tau). \tag{2.3}$$

Here the matrix $\mathbf{d}(\mathbf{q},\tau)$ depends only on the volume interaction of the linked units and on their low-molecular rearrangements; it therefore has the same form as for the corresponding broken-bond system.

With the approximation (2.2) we can write the partial contribution from molecular M to the collective response of the system as

$$-\Delta_i^{(M)}(\mathbf{r},t)=\frac{1}{V}\int_0^\infty d\tau\int dV'\alpha_{ij}^{(M)}(\mathbf{r}-\mathbf{r}',\tau)\tilde{\varepsilon}_j(\mathbf{r}',t-\tau), \tag{2.4}$$

where V is the volume of the system, and by analogy with (1.6) the molecular susceptibility $\boldsymbol{\alpha}^{(M)}$ of M is given by

$$\boldsymbol{\alpha}^{(M)}(\mathbf{q},p)=\boldsymbol{\Gamma}_M(\mathbf{q})-p\int_0^\infty\boldsymbol{\sigma}^{(M)}(\mathbf{q},t)\exp(-pt)\,dt. \tag{2.5}$$

Here

$$\begin{aligned}\sigma_{ij}^{(M)}(\mathbf{q},t)&=\int dV\langle\Delta_i^{(M)}(0,0)\Delta_j^{(M)}(\mathbf{r},t)\rangle\exp(i\mathbf{q}\mathbf{r})\\&=\sum\langle\exp\{i\mathbf{q}[\mathbf{r}_{\alpha_j}(t)-\mathbf{r}_{\beta_i}(0)]\}\rangle\end{aligned} \tag{2.6}$$

is the structure factor of macromolecule M, and $\Gamma_M(\mathbf{q})=\boldsymbol{\sigma}(\mathbf{q};t=0)$. The summation in (2.6) is over all units of types i and j belonging to M, and $\langle...\rangle$ denotes the usual statistical average taken over all states of M and the surrounding polymer material.

Recalling Eqs. (2.2)–(2.4), comparing Eqs. (1.3) and (2.1), and writing

$$\boldsymbol{\gamma}(\mathbf{q},p)=T\sum n_M\boldsymbol{\alpha}^{(M)}(\mathbf{q},p),$$

where n_M is the number of macromolecules of structure M per unit volume and the sum is over all types of structures (e.g., over all degrees of polymerization for linear chains), we obtain the desired relation

$$\boldsymbol{\alpha}^{-1}(\mathbf{q},p)=T[\boldsymbol{\gamma}^{-1}(\mathbf{q},p)-\mathbf{d}(\mathbf{q},p)]. \tag{2.7}$$

For $p=0$ this reduces to the expression derived by one of us in Refs. 15, 16 for the static polymer-density correlation functions:

$$\mathbf{G}^{-1}(\mathbf{q})=\mathbf{g}^{-1}(\mathbf{q})-\mathbf{c}(\mathbf{q}), \tag{2.8}$$

where the structure matrix

$$\mathbf{g}(\mathbf{q})=\sum n_M\boldsymbol{\Gamma}_M(\mathbf{q})$$

describes the structure-entropy effects (including linear memory), while the volume interaction is described by the direct correlation function matrix $\mathbf{c}(\mathbf{q})$, which is familiar from the theory of liquids.[17] It is therefore natural to refer to their generalizations $\boldsymbol{\gamma}(\mathbf{q},p)$ and $\mathbf{d}(\mathbf{q},p)$ to the time-dependent case as the structural and direct susceptibilities, respectively.

According to (2.7), the matrix $\boldsymbol{\alpha}^{-1}(\mathbf{q},p)$ is a sum of a structure-entropy and an energy contribution associated with the volume interaction. The physical significance of this additivity becomes clear if we note that according to (1.8), Eq. (2.8) implies that the respective contributions to the thermodynamic forces $\delta\mu_i/T$ are additive. On the other hand, we see using standard properties of the generalized susceptibility[3] that Eq. (2.7) expresses the fact that these contributions to the random forces $\{\varepsilon_i\}$ in Eq. (1.3) or (1.7) are statistically independent; the effect of these forces $\{\varepsilon_i\}$ can be described in terms of equivalent spontaneous fluctuations $\{\Delta_i\}$. Both of these properties follow natually from inequalities (1.1), which in our appoximation permit us to "decouple" the large- and the small-scale fluctuations. We will not discuss the generality of this approximation here (it corresponds to the random phase approximation) but merely note that it applies quite generally in the static case[5,16] [i.e., for Eq. (2.8) and the special cases derived previously by Edwards[18] and de Gennes[19]].

We now examine the structural and direct susceptibilities in more detail. It is easiest to derive the expression

$$\gamma_{ij}(q,p)=\sum_M n_M N_i^{(M)}N_j^{(M)}\,[1+(p/q^2D_M)]^{-1} \tag{2.9}$$

for the structural susceptibility in the macroscopic limit ($qR_M\ll1$, $pT_M\ll1$), where $N_i^{(M)}$ is the number of units of type i belonging to macromolecule M; according to Einstein's law, the corresponding diffusion coefficient D_M determines the mean-square displacement of the radius vector $\mathbf{R}(t)$ from the center of mass for large times: $\langle[\mathbf{R}(t)-\mathbf{R}(0)]^2\rangle=6D_Mt$. To derive (2.9) we must see $\mathbf{r}_i(t)\approx\mathbf{R}(t)$ in (2.5) and (2.6), neglect the macromolecular dimensions in comparison with the displacement of the macromolecule as a whole for $t\to\infty$, and recall that for a Gaussian random variable $R(t)$ we have

$$\langle\exp[i\mathbf{q}\mathbf{R}(t)]\rangle=\exp(-q^2\langle R^2(t)\rangle/6).$$

Compared with low-molecular systems, the values of N_i appearing in (2.9) are exceptionally large, and the small self-diffusion coefficients D_M explicitly reflect the polymer nature of the system.

In the Lifshits approach the direct susceptibility is calculated by applying Eq. (2.7) to a broken-bond system:

$$\mathbf{d}(q,p)=\boldsymbol{\gamma}_0^{-1}(q,p)-[T\boldsymbol{\alpha}_0(q,p)]^{-1}. \tag{2.10}$$

In general, $\boldsymbol{\alpha}_0$ and γ_0, the generalized and structural susceptibilities of the broken-bond system, are complicated functions of q and p; however, for relaxation processes in high polymers with $qr_0\ll1$, $pt_0\ll1$, it seems reasonable to neglect the dispersion to lowest order and set

$$d_{ij}(q,p)\approx d_{ij}(q=0,\ p=0)=\rho_{ij}^{-1}-T^{-1}(\partial\mu_i/\partial\rho_j)_T. \tag{2.11}$$

The last equality here is an exact thermodynamic relation; $\rho_{ij}=\bar\rho_i\delta_{ij}$ and μ_i is the chemical potential of the ith component of the broken-bond system (μ_i depends on the temperature and on the densities $\{\bar\rho_i\}$ of all the components). In particular, for a multicomponent lattice gas with the equation of state

$$\frac{vp}{T}=-\ln\varphi-{}^1/_2v^2k_{ij}\bar\rho_i\bar\rho_j,\qquad \varphi=1-\sum_{i=1}^{n}v\bar\rho_i,$$

where v and k_{ij} are parameters, we have

$$d_{ij}=v(k_{ij}-\varphi^{-1}); \tag{2.11a}$$

the last term becomes infinite as $\varphi\to0$ and ensures that the entire system is incompressible in the limit $\varphi\to0$, i.e., $p/T\to\infty$. In this limit the theory for two-component systems becomes particularly simple; if we substitute (2.11a) into Eq. (2.7) and let $\varphi\to0$, we get

$$T\alpha_{ij}(q,p)=T\alpha(q,p)(2\delta_{ij}-1)=\frac{2\delta_{ij}-1}{\tilde\gamma^{-1}(q,p)-2\chi v}, \tag{2.12}$$

where the Flory-Higgins parameter[9] $2\chi=k_{11}+k_{22}-2k_{12}$ characterizes the interaction of the broken monomer units, and $\tilde\gamma^{-1}=(\gamma^{-1})_{11}+(\gamma^{-1})_{22}-2(\gamma^{-1})_{12}$. If we use expression (2.12) for the generalized susceptibility, the definitions (1.6)–(1.8) yield the linear relaxation equation

$$\frac{\partial}{\partial t}\Delta(q,t)=-q^2\int_0^\infty d\tau\Lambda(q,\tau)G^{-1}(q)\Delta(q,t-\tau) \tag{2.13}$$

and the expression

$$\sigma_{ij}(q,\omega)=\int_{-\infty}^{\infty}dtS_{ij}(q,t)\exp(i\omega t)=\sigma(q,\omega)(2\delta_{ij}-1),$$

$$\sigma(q,\omega)=2\frac{q^2G^2(q)\operatorname{Re}\Lambda(q,\omega)}{|q^2\Lambda(q,p=i\omega)+i\omega G(q)|^2} \tag{2.14}$$

for the dynamic form-factor. Here the bond density fluctuations $\Delta(\mathbf{r},t)$ is the same for all the components of the system,

$$G(q)=T\alpha(q,\quad p=0)=[\tilde g^{-1}(q)-2\chi v]^{-1},$$

$$\tilde g^{-1}=(g^{-1})_{11}+(g^{-1})_{22}-2(g^{-1})_{12},$$

and the kinetics coefficient is given by

$$\frac{p\Lambda^{-1}(q,p)}{q^2}=\frac{\alpha^{-1}(q,p)}{T}-G^{-1}(q)=\tilde\gamma^{-1}(q,p)-\tilde g^{-1}(q). \tag{2.15}$$

We see from (2.15) that even in the diffusion (macroscopic) region for which the structural susceptibility is described by the limiting expression (2.9), the frequency dispersion of the kinetic coefficients can vanish only if at most two types of macromolecules are present in the system. In this case Eq. (2.13) reduces to the Fick equation

$$\frac{\partial}{\partial t}\Delta(q,t)=-q^2D_{\text{coop}}\Delta(q,t), \tag{2.13a}$$

where

$$D_{\text{coop}}=\frac{(\varphi_1N_1)^{-1}+(\varphi_2N_2)^{-1}-2\chi(x_1-x_2)^2}{(\varphi_1N_1D_1)^{-1}+(\varphi_2N_2D_2)^{-1}} \tag{2.16}$$

is the cooperative diffusion coefficient. Here $\varphi_i=vn_iN_i=v\bar{\rho}_i$ is the volume fraction of all the linked units belonging to macromolecules of type i with self-diffusion coefficient D_i and degree of polymerization N_i; $x_i=N_i^A/N_i$ is the fraction of type-A units contained in macromolecules of type i. Expression (2.16) generalizes the result derived in Refs. 8 and 20 for binary homopolymer mixtures with $|1-2x_i|=1$.

However, for systems containing three or more different types of macromolecules the kinetic coefficient (2.15) is subject to considerable dispersion; we analyzed some of the consequences of this in Ref. 21 for the diffusion-dominated case. In what follows we will consider some characteristic effects for the fluctuation-dominated case $qR_M\gtrsim 1$, $pT_M\gtrsim 1$.

3. MOLECULAR SUSCEPTIBILITY OF A REPTATING POLYMER CHAIN AND THE FREQUENCY DISPERSION OF THE KINETIC COEFFICIENT

The short-range repulsion between the polymer chains has two consequences. First, there is a maximum packing density $\rho_{\max}=v^{-1}$, which we have allowed for by introducing the phenomenological parameter v in (2.11a) and in the equation of state for the broken-bond system. The second consequence, which cannot be treated in this way, is that the polymer chains cannot cross one another; this "topological interaction" shows up most certainly as conservation of the topological invariants of the closed polymer chains.[10,11] The topological interaction has no influence on the equilibrium properties of a system of linear (unclosed) chains, for which all points in configuration space are topologically equivalent; however, it can greatly alter the dynamic behavior of such a system at finite times. For example, if the topological interaction is strong enough, each chain will be so tightly "squeezed" by its neighbors that it can move only by "reptating," i.e., by creeping along its edges.[9]

According to Doi and Edwards,[22] polymer chains reptation can be regarded as a random walk of an incompressible nondetachable flexible chain inside an empty cage in a crystal lattice with a large coordination number. The Langevin equation is simplest if we take the random walk to be discrete:

$$\boldsymbol{\rho}_n(t+\Delta t)=\frac{1+\xi(t)}{2}\boldsymbol{\rho}_{n+1}(t)+\frac{1-\xi(t)}{2}\boldsymbol{\rho}_{n-1}(t). \tag{3.1}$$

Here $\boldsymbol{\rho}_n(t)=\mathbf{R}(na,t)-\mathbf{R}((n-1)a,t)$, where a is the distance between the nearest-neighbor lattice sites, and $\mathbf{R}(s,t)$ is the radius vector of a point on the chain lying a distance s (measured along the chain) from the end of the chain at time t; the random variable $\xi(t)$ takes the values ± 1 with equal probability and gives the direction of movement of the chain; Δt is the time required for one reptation step, during which each point moves a distance a and occupies the site formerly filled by one of its two neighbors. For a chain of length $L=(N-1)a$, Eq. (3.1) must be solved subject to the boundary conditions

$$\boldsymbol{\rho}_0(t)=a\mathbf{v}_0(t),\quad \boldsymbol{\rho}_N(t)=a\mathbf{v}_N(t), \tag{3.2}$$

where the random unit vector $\mathbf{v}_\alpha$ $(\alpha=0,N)$ points with equal probability to either of the two unoccupied sites nearest the corresponding end (α) of the chain.

The mathematical model of reptation given by Eqs. (3.1) and (3.2) yields fairly simple expressions for the molecular characteristics (2.5) and (2.6). To derive them we must use (3.1) and (3.2) to obtain the analogous dynamic equation and boundary conditions for the quantity $\exp\{i\mathbf{q}[\mathbf{r}_i(t)-\mathbf{r}_j(0)]\}$ and then average over all chain configurations and values of the random variables. Passing from difference to differential equations, we obtain[22]

$$\frac{\partial g}{\partial t}=D\frac{\partial^2 g}{\partial s_2},\quad \frac{\partial g}{\partial s}=\begin{cases}-\varkappa g, & s=0\\ \varkappa g, & s=L\end{cases}. \tag{3.3}$$

Here

$$g(s,s';q,t)=\langle\exp\{i\mathbf{q}[\mathbf{R}(s,t)-\mathbf{R}(s',0)]\}\rangle,\quad \varkappa=q^2a/6,$$

is the diffusion coefficient of the chain as a whole inside an unbounded tube, and we can write $D=a^2/\Delta t$ as $D=D_0/N$, where the phenomenological parameter D_0 is comparable in order of magnitude to the self-diffusion coefficient of the broken bonds. Equations (3.3) with the initial conditions[5,9]

$$g(s,s';q,t=0)=\exp(-\varkappa|s-s'|) \tag{3.4}$$

can be solved by the standard method[22]; the result can be expressed most simply in terms of the Laplace transform:

$$\begin{aligned}g(s,s';q,p)&=\int_0^\infty dt g(s,s';q,t)\exp(-pt)\\ &=\frac{\mu}{\mu^2-P}\left\{\frac{\exp(-P^{1/2}|\theta-\theta'|)}{P^{1/2}}-\frac{\exp(-\mu|\theta-\theta'|)}{\mu}\right\}\\ &\quad-\frac{\mu\exp(-P^{1/2})}{P^{1/2}(\mu+P^{1/2})}\\ &\quad\times\left\{\frac{\operatorname{ch}(P^{1/2}\theta)\operatorname{ch}(P^{1/2}\theta')}{P^{1/2}\operatorname{sh}(P^{1/2})+\mu\operatorname{ch}(P^{1/2})}+\frac{\operatorname{sh}(P^{1/2}\theta)\operatorname{sh}(P^{1/2}\theta')}{P^{1/2}\operatorname{ch}(P^{1/2})+\mu\operatorname{sh}(P^{1/2})}\right\}.\end{aligned} \tag{3.5}$$

Here we have introduced the dimensionless variables

$$\theta=(2s-L)/L,\quad \mu=q^2R^2/2,\quad P=p\tau/2,$$

where $R^2=aL/6=Na^2/6$ is the mean-square inertial radius and $\tau=N^2a^2/2D=N^3a^2/2D_0$ is the characteristic time for the center of mass of the macromolecule to move by an average distance comparable to the molecular dimension R. On the other hand, this time is just $\tau=R^2/D_N$, where D_N is the self-diffusion coefficient of a chain reptating in space, so that we find the expression

$$D_N=D/3N=D_0/3N^2. \tag{3.6}$$

The self-diffusion coefficient D in (3.6) for a chain in an unbounded tube contains an extra factor of $1/N\ll 1$; this re-

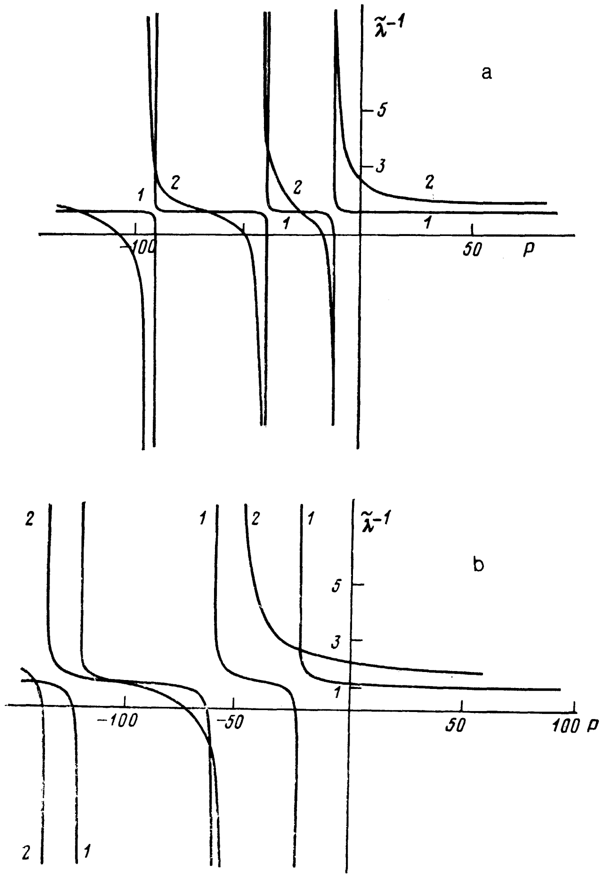

FIG. 1. Frequency dispersion characteristic of the kinetic coefficient. Numerically calculated values $\tilde{\lambda}^{-1}(P) = \lambda_\infty(\mu)/\lambda(\mu,P)$ are plotted for $\mu = 1$ (curves 1) and $\mu = 10$ (curves 2) as a function of the variable $P = p\tau/2$ for an $A_N + B_N$ mixture (a) and for a diblock copolymer A_NB_N (b).

flects the important fact that it is only the random walk along the tube that is Gaussian—the random walk of the chain in space is statistically more complicated because of the additional averaging over the different trajectories of the tube.

The expressions for the static and dynamic molecular factors follow by substituting (3.4) and (3.5) respectively into the definition

$$\sigma_{ij}(q) = \frac{1}{a^2}\int_0^L ds \int_0^L ds' g(s,s';q)\,\delta_i(s)\,\delta_j(s'), \qquad (3.7)$$

where the function $\delta_i(s)$ is equal to 1 if the point s corresponds to a bond of type i and is zero otherwise. For the special case of a homopolymer A_N with $\delta_A(s) = 1$ and $\delta_{17A}(s) = 0$, we can evaluate the integrals and substitute them into (2.5) to get the molecular susceptibility

$$vT\alpha^{(N)} = \frac{\varphi_N N \mu^2}{\mu^2 - P}\left\{\frac{1}{P + \mu P^{1/2}\,\mathrm{cth}(P^{1/2})} - \frac{1}{\mu^2(1 + \mathrm{cth}\,\mu)}\right\}, \qquad (3.8)$$

where φ_N is the volume fraction of the polymer A_N. For a mixture of two homopolymers A_{N_1} and B_{N_2} with volume fractions φ_1 and $\varphi_2 = 1 - \varphi_1$, this leads to the following expressions for the static correlation function G_q and the kinetic coefficient (2.15):

$$vG_q = \left\{\sum_{i=1}^{2}[\varphi_i N_i f(\mu_i)]^{-1} - 2\chi\right\}^{-1}, \qquad (3.9)$$

$$v\Lambda(q,p) = \left\{\sum_{i=1}^{2}[\varphi_i N_i D_i \lambda_\infty(\mu_i)]^{-1}[1 + F(\mu_i, P_i)]\right\}^{-1}. \qquad (3.10)$$

Here

$$\mu_i = q^2R_i^2/2, \quad P_i = p\tau_i/2, \quad f(\mu) = \mu^{-1} - \mu^{-2}(1 + \mathrm{cth}\,\mu)^{-1},$$
$$D_i = D_0/3N_i^2, \quad \lambda_\infty^{-1}(\mu) = \mu(1 + \mathrm{cth}\,\mu),$$
$$F(\mu,P) = f^{-1}(\mu)\,\frac{(\mu^2/P)[P^{1/2}\,\mathrm{cth}(P^{1/2}) - 1] + 1 - \mu\,\mathrm{cth}\,\mu}{\mu^2(1 + \mathrm{cth}\,\mu) - P - \mu P^{1/2}\,\mathrm{cth}(P^{1/2})}. \qquad (3.11)$$

Expression (3.9) is familiar from the theory of polymers,[9,15] but (3.10) differs from Pincus's result[7] and more closely resembles Binder's last expression,[8] in that both expressions contain functions $F(\mu,P)$ which explicitly describe the frequency dispersion of the kinetic coefficient in the fluctuation region. According to (3.11), $F(\mu,P)$ vanishes as $p \to \infty$, so that our result agrees with Pincus's in this limit. This has a simple physical explanation—the analyses in Refs. 6–8 all assumed that the effective field $\tilde{\varepsilon}$ was equal to the external field ε, which as shown in Sec. 2 is not true in general. Nevertheless, the molecular fields (2.3) which determine the difference between $\tilde{\varepsilon}$ and ε are still small immediately after the external fields have been turned on, so that at sufficiently high frequencies the responses of the macromolecules are mutually independent and depend solely on the external fields. (We note that the Pincus result[7] is the only one that gives the correct asymptotic behavior of the kinetic coefficient in the limit $p \to \infty$).

We can also use Eqs. (3.4), (3.5), and (3.7) to find the molecular characteristics for heteropolymer chains, i.e., for linear macromolecules containing several different types of bonds. Because these results are cumbersome to write out, we will consider only the simplest case of a symmetric diblock copolymer consisting of macromolecules $A_{IV}B_{IV}$ in which two homopolymer chains (blocks) A_{IV} and B_{IV} are joined by a chemical bond A–B:

$$v\tilde{\gamma} = {}^1/_4 N\mu[u(\mu,P) + \psi(\mu)](\mu^2 - P)^{-1},$$
$$v\Lambda = ND_{2N}\psi(u + \psi)[\psi + (\mu^2/P)u]^{-1}, \qquad (3.12)$$
$$u(\mu,P) = \frac{1}{2}\left\{1 - \frac{1 + \mu\,\mathrm{th}(P^{1/2}/2)/(P^{1/2}/2)}{\mu + P^{1/2}\,\mathrm{cth}(P^{1/2})}\right\},$$
$$\psi = -u(\mu, P = \mu^2),$$

where

$$\mu = (2N)q^2a^2/12, \quad P = p(2N)^3a^2/12D_0.$$

We see from (3.12) that the static correlation function

$$G(q) = N/v[f^{-1}(\mu) - 2\chi N],$$
$$f(\mu) = [2\mu - (3 - e^{-\mu})(1 - e^{-\mu})]/4\mu^2 \qquad (3.13)$$

for a symmetric diblock copolymer has a maximum at the finite value $\mu \approx 1.9$ (Refs. 12, 13). The spinodal of this system (reached for $\chi = \chi_c \approx 5.25/N$) therefore corresponds to a loss of thermodynamic equilibrium which does not involve stratification into two unbounded phases but instead is accompanied by the formation of a spatially nonuniform phase for which the "order parameter" $\Delta(\mathbf{r})$ possesses a crystal lattice symmetry.[12,23] Stratification does not occur because the thermodynamically incompatible blocks are held together by chemical bonds. Although in this respect the correlation function (3.13) for the heteropolymer differs radically from G_q in (3.9) for a homopolymer mixture (melt), which peaks at $\mu = 0$, the qualitative behavior of the kinetic coefficients is the same for both systems (Fig. 1). According to Eqs. (3.10)–(3.12), the behavior of the reduced kinetic coefficient

$$\lambda(\mu,P)=\frac{v\Lambda(\mu,P)}{\varphi_1\varphi_2 ND_N},\quad \frac{v\Lambda(\mu,P)}{ND_{2N}}\tag{3.14}$$

shown in Fig. 1 is described for $\mu \gg 1$ and $P \geqslant 0$ by the asymptotic expressions

$$\tilde{\lambda}=\frac{\lambda(\mu,P)}{\lambda_\infty(\mu)}$$

$$=\begin{cases}\dfrac{2P/\mu}{P^{1/2}\operatorname{cth}(P^{1/2})-1},\ \dfrac{2P/3\mu}{{}^1/_2P^{1/2}\operatorname{cth}(P^{1/2}/2)-1}, & P\ll\mu^2,\\ 1-(\mu^2/P)+\ldots,\ 1-(2\mu/3P^{1/2})+\ldots, & P\gg\mu^2,\end{cases}\tag{3.14a}$$

$$\lambda_\infty(\mu)=\frac{1}{\mu(1+\operatorname{cth}\mu)},\quad \frac{1+2\operatorname{th}(\mu/2)}{2\mu(1+\operatorname{cth}\mu)},\tag{3.15}$$

where the first column on the right gives the result for a symmetric melt consisting of homopolymers A_N and B_N, while the second column refers to a symmetric block copolymer $A_N B_N$. As might have been expected, the kinetic coefficient becomes less sensitive to P as μ becomes smaller, and for a homopolymer μ is virtually independent of P when $\mu \lesssim 1$ and $P \geqslant 0$. However, for the block copolymer a small but finite frequency dispersion persists even in the limit $\mu \to 0$:

$$\lambda(0,\ P)/\lambda(0,\ \infty)=\{[1-(\operatorname{th}(P^{1/2})/P^{1/2})]^{-1}-3/P\}^{-1}.\tag{3.16}$$

This residual dispersion in the diffusion-dominated regime is present because the different blocks are chemically linked into a single macromolecule. An even more important property may be noted—for both systems the analytic function $\lambda(q,P)$ of the complex variable P has infinitely many zeros and poles which lie on the negative axis $P<0$ at a finite distance from the origin $P=0$. We will see below that this structure of $\lambda(q,P)$ reflects the fact that when the topological interaction among the chains is strong, no relaxation process can occur faster than the chains can "untangle".

4. FREQUENCY DEPENDENCE OF THE DYNAMIC FORM-FACTOR

In this section we derive asymptotic expressions for the dynamic form-factor $\sigma(q,\omega)$ for polymer melts (σ can be measured in x-ray and neutron scattering experiments). The derivation is simplest for symmetric systems (for a diblock copolymer $A_N B_N$ or a mixture of homopolymers A_N and B_N). In this case we have

$$\tilde{\sigma}=\frac{\sigma(q,\omega)}{G(q)\tau}=\operatorname{Re}\{i\Omega+\mu\lambda(\mu,i\Omega)(f^{-1}(\mu)-\tilde{\chi})\}^{-1},\tag{4.1}$$

where $\Omega = \omega\tau/2$, and $\tilde{\chi} = 2\chi N\Phi_1\Phi_2$ for a homopolymer mixture and $\tilde{\chi} = 2\chi N$ for a heteropolymer. The results in the previous section lead to the asymptotic expressions

$$\tilde{\sigma}(\mu,\Omega)=\begin{cases}\psi_1(\Omega), & {}^1/_4\psi_1(\Omega/4), & \Omega\ll\mu^2,\\ \mu/2\Omega^2, & 3\mu/2\Omega^2, & \Omega\gg\mu^2,\end{cases}\tag{4.2}$$

which are valid for $\mu \gg \max(1,|\tilde{\chi}|)$; here and below we use the same double-column notation as in Eqs. (3.14), and

$$\psi_1(x^2)=(\operatorname{sh}x-\sin x)/2x^3(\operatorname{ch}x+\cos x).$$

The qualitative behavior is the same for both systems, because the presence or absence of bonds between the units plays virtually no role over distances small compared to the dimensions of the units. On the other hand, the behavior is completely different for long wavelengths $\mu \ll 1$. The homopolymer is described by the ordinary Lorenz expression for the dynamic form-factor:

$$\tilde{\sigma}=\Gamma/(\Omega^2+\Gamma^2),\quad \Gamma(\mu)=\mu[\varepsilon+2\mu/3+\ldots],\tag{4.3}$$

whose halfwidth $\Gamma(\mu)$ as a function of μ corresponds to ordinary diffusion (corrected for the thermodynamic retardation near the spinodal, where $\varepsilon = 1 - \chi \to 0$). On the other hand, in the long-wavelength limit the block copolymer is described by the form-factor

$$\tilde{\sigma}=\frac{3}{\Omega^2}\left\{1-\frac{1}{(2\Omega)^{1/2}}\frac{\operatorname{sh}[(2\Omega)^{1/2}]+\sin[(2\Omega)^{1/2}]}{\operatorname{ch}[(2\Omega)^{1/2}]+\cos[(2\Omega)^{1/2}]}\right\},\tag{4.4}$$

which is independent of μ. This unorthodox behavior is due in part to the reptation dynamics of the chains and in part to the assumption that the system is incompressible and all the macromolecules have identical structures, so that any macroscopic inhomogeneity in the composition relaxes over times comparable to the untangling time of the chains. Another interesting type of behavior occurs when the units A and B are thermodynamically highly compatible and

$$\tilde{\chi}<0,\quad 1\ll\mu\ll|\tilde{\chi}|.\tag{4.5}$$

In this case, three regimes occur when $\mu^2 \gg |\tilde{\chi}|$:

$$\tilde{\sigma}=\begin{cases}(\mu/|\tilde{\chi}|)\psi_2(2\Omega),\ (\mu/4|\tilde{\chi}|)\psi_2(\Omega/2),\ \Omega\ll\tilde{\chi}^2/\mu^2, & (4.6a)\\ |\tilde{\chi}|/\mu(2\Omega^3)^{1/2},\ |\tilde{\chi}|/\mu(\Omega^3/2)^{1/2},\ \mu^2\gg\Omega\gg\tilde{\chi}^2/\mu^2, & (4.6b)\\ |\tilde{\chi}|/[2\Omega^2+(\hat{\chi}^2/2)],\ 3|\tilde{\chi}|/[4\Omega^2+(3\tilde{\chi}/2)^2],\ \Omega\gg\mu^2. & (4.6c)\end{cases}$$

If $\mu^2 \ll |\tilde{\chi}|$, the regimes (4.6a) and (4.6c) coalesce near $\Omega \sim \mu^2$ at the expense of (4.6b), which disappears. In Eq. (4.6a)

$$\psi_2(x^2)=(\operatorname{sh}x-\sin x)/x(\operatorname{ch}x-\cos x).$$

The behavior of σ for an asymmetric mixture of homopolymer chains A_{N_1} and B_{N_2} with $N_1 \neq N_2$ is much more complicated. First of all, the molecular characteristics of both mixture components must be suitably averaged in order to obtain the natural scaling parameters R and τ in this case, and the method of averaging depends on the regime considered. For example, expression (4.3) with

$$R^2=N_{\text{eff}}a^2/6,\quad N_{\text{eff}}=N_1N_2/(\varphi_1N_1+\varphi_2N_2),\quad \tau=R^2/D_{\text{eff}},\tag{4.7}$$

describes the behavior in the long-wave (diffusion) case, where the diffusion coefficient D_{eff} is given by (2.16). On the other hand, in the short-wave (high-frequency) limit (4.2), D_{eff} in (4.7) is given by the formula

$$D_{\text{eff}}=D_1D_2/(\varphi_1D_1+\varphi_2D_2). \tag{4.8}$$

A second complication arises from the fact that the parameters N_2/N_1 may be small, so that additional regimes may occur (e.g., $\mu_2 \ll 1, \mu_2 \gg 1$). We will not pause here to analyze this further; the corresponding expressions can be derived in exactly the same way as Eqs. (4.2)–(4.8).

5. TIME RELAXATION IN POLYMER MELTS

In many experiments one does not measure the frequency dependence of the dynamic form-factor but rather studies the time-evolution directly, where the time is measured from the instant when an inhomogeneous composition distribution $\Delta_0(\mathbf{r})$ has been achieved by some artificial means. Let us assume for definiteness that the distribution $\Delta_0(\mathbf{r})$ has relaxed due to the effects of an external field $\varepsilon(\mathbf{r})$ which is turned off at time $t = 0$ after having acted for arbitrarily long times $-\infty < t < 0$. Then the relaxation equation (1.7) implies that

$$\Delta(\mathbf{r},t)=\int\frac{dp}{2\pi i}\int\frac{d^3q}{(2\pi)^3}\Delta(p,\mathbf{q})\exp(pt-i\mathbf{qr}), \tag{5.1}$$

$$\Delta(p,q)=\Delta_0(q)\,[p+q^2\Lambda(q,p)G^{-1}(q)]^{-1}, \tag{5.2}$$

where (5.1) is the definition of the inverse Fourier-Laplace transform, and

$$\Delta_0(q)=\int dV\Delta_0(\mathbf{r})e^{i\mathbf{qr}}.$$

As in Sec. 4, we begin with symmetric systems, for which (5.2) reduces to the expression

$$\Delta(P,\mu)={}^1/_2\Delta_0(\mu)\tau\{P+\mu\lambda(\mu,P)\,[f^{-1}(\mu)-\tilde{\chi}]\}^{-1} \tag{5.3}$$

analogous to (4.1). Using standard properties of the Laplace transform[24] and recalling the properties of the function $\lambda(\mu,P)$ in Sec. 3, we get the asymptotic expressions

$$w(t)=\frac{\Delta(\mu,t)}{\Delta_0(\mu)}=\begin{cases}1-\Gamma_0\tilde{t}+\ldots, & \Gamma_0\tilde{t}\ll 1, \quad (5.4\text{a})\\ A\exp(-\Gamma_\infty\tilde{t}), & \Gamma_\infty\tilde{t}\gg 1, \quad (5.4\text{b})\end{cases}$$

for the relaxation function $w(t)$, where

$$\tilde{t}=2t/\tau, \quad \Gamma_0=\mu\lambda_\infty(\mu)\,[f^{-1}(\mu)-\tilde{\chi}], \quad \Gamma_\infty=-P_0,$$

and P_0 is the largest of the (real negative) roots of the equation

$$P+\mu\lambda(\mu,P)\,[f^{-1}(\mu)-\tilde{\chi}]=0. \tag{5.5}$$

The graphical solution of (5.5) is shown in Fig. 2 for two different cases; we see that the inequalities

$$\Gamma_\infty(\mu)<\Gamma_0(\mu), \text{ and } \Gamma_\infty(\mu)<\bar{\Gamma}(\mu). \tag{5.6}$$

are satisfied. According to the first inequality, the frequency dispersion retards the time relaxation. This is because the molecular field ε^* has a nonzero relaxation time; we recall from our discussion of Eqs. (3.10), (3.11) that this field ensures that the independent random motions of the various macromolecules, which initially are statistically independent, become highly correlated as required by the high density of the system. Although this observation holds quite generally, the consequences for polymers may be particularly important because the reptation dynamics of the chains differs from the case of a Gaussian random walk. In particular, the second inequality in (5.6) shows that regardless of the initial value $w(0)$, for very large times the relaxation rate $w(t)$ is limited by the rate at which the reptating chains can untangle. We note the $\bar{\Gamma}$, defined as the (negative real) zero of $\lambda(\mu,P)$ lying closest to the origin, lies in the interval $\pi^2 < \bar{\Gamma}(\mu) < \pi^2(1+\delta)$, where $\delta \approx 0.1$, as follows from a numerical analysis of Eq. (3.11).

In the diffusion limit ($\mu \ll 1$) λ_∞ and $\lambda(0)$ are nearly equal ($\lambda_\infty - \lambda(0) \sim \mu^2\lambda_\infty$) for mixtures of homopolymers, and unless the thermodynamic interaction parameter $\tilde{\chi}$ is very large, the usual diffusion relaxation occurs:

$$w(t)=\exp(-\Gamma_0\tilde{t}), \quad \Gamma_0(\mu)=\mu(1-\tilde{\chi})+2\mu^2/3+\ldots. \tag{5.7}$$

Even here, however, the initial relaxation rate Γ_0 may be much greater than $\bar{\Gamma}$ if

$$1\gg\mu\gg(-\tilde{\chi})^{-1}, \tag{5.8}$$

as may occur for mixture components with a high degree of thermodynamic compatibility. In this case the relaxation function can be written as

$$w(t)=\exp(-\Gamma_0\tilde{t})+f_1(\tilde{t}), \tag{5.9}$$

where the Laplace transform of the function $f_1(\tilde{t})$ and its limiting behavior are given by

$$f_1(P)=F(\mu,P)\Gamma_0/[P\tilde{\lambda}^{-1}(\mu,P)+\Gamma_0]\,(P+\Gamma_0), \tag{5.10}$$

$$f_1(\tilde{t})=\frac{\mu}{3|\tilde{\chi}|}\begin{cases}1-6(\tilde{t}/\pi)^{1/2}+\ldots, & \Gamma_0^{-1}\ll\tilde{t}\ll 1, \quad (5.11\text{a})\\ (6/\pi^2)\exp(-\pi^2\tilde{t}), & \tilde{t}\gg 1. \quad (5.11\text{b})\end{cases}$$

The reptation dynamics of the polymers shows up here as a small residual relaxation (of order $\sim\mu/|\chi|$) which is described by $f_1(t)$ and has the characteristic time τ.

When $\mu \gg 1$, the behavior of $w(t)$ for homopolymer mixtures also depends on the ratio $\mu/\tilde{\chi}$, but in a more complicated way. Three situations can occur: A) $|\tilde{\chi}| \ll \mu$; B) $\mu \ll |\tilde{\chi}| \ll \mu^2$; C) $\mu^2 \ll |\tilde{\chi}|$.

In case A

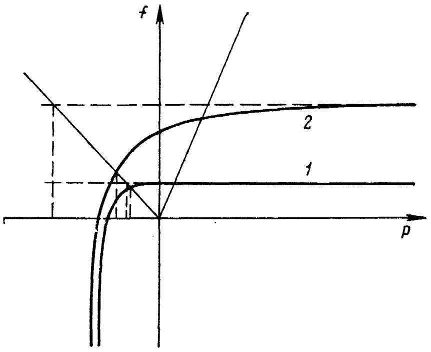

FIG. 2. Graphical derivation of inequalities (5.6). Curves 1 ($\mu \lesssim 1$) and 2 ($\mu \gg 1$) and their asymptotes (dashed) show $\mu\lambda(P)/G$ and $\mu\lambda_\infty(P)/G$, respectively. These curves intersect the line $f = -P$ at $P = \Gamma_\infty(\mu)$ and $P = \Gamma_0(\mu)$, respectively, and their positive intercepts with the line $f = +P$ determine how rapidly the composition becomes nonuniform when $G^{-1}(\mu) < 0$, i.e., during the initial stage of spinodal decay of the system[6–8] (which we do not consider in this paper).

$$w(t)=\begin{cases} 1-(\mu\tilde{t}/2)+\ldots, & \tilde{t}\ll\mu^{-2}, \quad (5.12a)\\ 1-2(\tilde{t}/\pi)^{1/2}+\ldots, & \mu^{-2}\ll\tilde{t}\ll 1, \quad (5.12b)\\ (2/\pi)^3\exp(-\pi^2\tilde{t}/4), & \tilde{t}\gg 1. \quad (5.12c)\end{cases}$$

We observe that for $\tilde{t}\ll\mu^{-2}$, (5.12a) agrees with Pincus's result,[7] while the asymptotic expressions (5.12b) and (5.12c) correspond to features of individual chain reptation that were analyzed by De Gennes.[25] In case B, the relaxation is much more rapid and occurs in four stages with the asymptotic behavior

$$w(t)=\begin{cases} 1-|\tilde{\chi}|\tilde{t}/2+\ldots, \quad \tilde{t}\ll\mu^{-2}, & (5.13a)\\ 1-2(|\tilde{\chi}|/\mu)(\tilde{t}/\pi)^{1/2}+\ldots, \quad \mu^{-2}\ll\tilde{t}\ll\mu^2/\tilde{\chi}^2, & (5.13b)\\ (\mu/|\tilde{\chi}|)(\pi\tilde{t})^{-1/2}, \quad \mu^2/\tilde{\chi}^2\ll\tilde{t}\ll 1, & (5.13c)\\ 2(\mu/|\tilde{\chi}|)\exp(-\pi^2\tilde{t}), \quad \tilde{t}\gg 1. & (5.13d)\end{cases}$$

Finally, in case C the relaxation can be expressed in a form analogous to (5.9):

$$w(t)=\exp(-\Gamma_0\tilde{t})+f_2(\tilde{t}), \quad \Gamma_0=|\tilde{\chi}|/2, \tag{5.14}$$

$$w(t)=\frac{2\mu^2}{|\tilde{\chi}|}\begin{cases} 1-4(\mu^2\tilde{t}/\pi)^{1/2}+\ldots, \quad \Gamma_0^{-1}\ll\tilde{t}\ll\mu^{-2}, & (5.14a)\\ (\pi/4\mu^2\tilde{t})^{1/2}, \quad \mu^{-2}\ll\tilde{t}\ll 1, & (5.14b)\\ \mu^{-1}\exp(-\pi^2\tilde{t}), \quad \tilde{t}\gg 1. & (5.14c)\end{cases}$$

We have already noted in Sec. 4 that for $\mu\gg 1$, the behavior of $w(t)$ for a block copolymer is essentially identical to that described above. One can show that Eqs. (5.12)–(5.14) continue to hold, provided that $\tilde{t}$ is replaced by $3\tilde{t}$ in (5.12a), (5.13a), and (5.14a) and by $4\tilde{t}$ elsewhere. However, $w(t)$ becomes independent of μ in the limit $\mu\to 0$ and behaves as

$$w(\tilde{t})=\begin{cases} 1-3\tilde{t}+4\tilde{t}^{3/2}/\pi^{1/2}, & \tilde{t}\ll 1, \quad (5.15a)\\ 3(2/\pi)^5\exp(-\pi^2\tilde{t}/4), & \tilde{t}\gg 1. \quad (5.15b)\end{cases}$$

These expressions correspond to Eq. (4.4) for the dynamic form-factor. On the other hand, a slow damping of fluctuations with $\Gamma_\infty\ll 1$ analogous to (5.7) is observed only for fluctuations whose wave number is close to the critical value $\mu_0\approx 1.9$ at which the static correlation function (3.13) peaks; this occurs near the spinodal, at which $\varepsilon=2N(\chi_c-\chi)\ll 1$. In this case

$$\Gamma_0\approx 1.2\Gamma_\infty, \tag{5.16a}$$

$$\Gamma_\infty\approx 0.5[\varepsilon+(\mu-\mu_0)^2]. \tag{5.16b}$$

The above analysis generalizes easily to asymmetric mixtures of homopolymers A_{N_1} and B_{N_2} with $N_1>N_2$. If the system is nearly symmetric ($x=N_2/N_1\sim 1$), all of the above results hold except that the characteristic scales τ and R now depend on the composition; they are of order unity and in general differ for the different regimes (cf. Sec. 4). The case of strong asymmetry $x\ll 1$ is of greater interest and can be analyzed using the reptation model only when $\varphi_2\ll 1$, i.e., when only a few short chains (impurities) are present and the topological interaction among the long chains determines the reptation mechanism. In this case only inhomogeneities with $\mu_2\ll 1$ are of physical interest, and the frequency dispersion of the kinetic coefficient for the short impurity chains can be neglected. Substitution of (3.9) and (3.10) into (5.2) then yields

$$w(p)={}^1/_2\tau_1\{P_1-\mu_1[\lambda^{-1}(\mu_1, P_1)+(x/\varphi_2)]^{-1}\tilde{\chi}\}^{-1}, \tag{5.17}$$

where the effective interaction parameter

$$\tilde{\chi}=2\chi N_1-(x\varphi_2)^{-1} \tag{5.18}$$

increases in absolute value as the concentration and degree of polymerization of the mixture decrease. If the impurity concentration is not too low, so that the behavior of the relaxation function is determined by values of p for which

$$\varphi_2\gg x\lambda(\mu_1, P_1), \tag{5.19}$$

$w(t)$ is given by the expressions derived above for a symmetric mixture, provided $\tilde{\chi}$ is defined by (5.18). If $\varphi_2\ll x\lambda(\mu_1,P_1)$ and $\mu\ll x^2$, then

$$w(t)=\exp[-q^2D_2t(1-2\chi\varphi_2N_2)]. \tag{5.20}$$

In other words, for low impurity concentrations self-diffusion (the statistically independent random walks of the molecules) is responsible for the slow (long-wave) relaxation. However, in all cases when the initial relaxation rate

$$\Gamma_0=\mu|\tilde{\chi}|[\mu(1+\operatorname{cth}\mu)+(x/\varphi_2)]^{-1} \tag{5.21}$$

is large compared to 1, the residual reptation relaxation depends on the impurity concentration solely because of the dependence of the parameter $\tilde{\chi}$, and it is described by the above formulas.

6. CORRECTIONS FOR IMPURITIES AND A SMALL DEGREE OF COMPRESSIBILITY

Because of the laws of equilibrium thermodynamics and the conditions under which polymer systems are formed, the macromolecules inevitably vary greatly in size and some monomers are present. The size distribution is typically exponential: $n(N)=\overline{N}^{-1}\exp(-N/\overline{N})$, where $n(N)$ is the number of N-mers. Because the monomers are much more mobile than the N-mers for large N, there may be some doubt whether the results derived above for model systems of only two types of macromolecule apply to real systems. A qualitative answer can be found by considering a system consisting of three different chains A_{N_1}, A_{N_2}, and B_M, where A_{N_2} (with $N_2\ll N_1$) is the impurity. The expression

$$\begin{aligned}(v\Lambda(\mathbf{q}, p))^{-1}&=[\varphi_B N_B D_B\lambda(P_B, \mu_B)]^{-1}\\ &+[\varphi_1 N_1 D_1\lambda(P_1, \mu_1)]^{-1}[1+(p/q^2D_2)]/\{1\\ &+(p/q^2D_2)[1+(xyD_2/D_1\lambda(P_1\mu_1)]\}\end{aligned} \tag{6.1}$$

for the kinetic coefficient $\Lambda(\mathbf{q},p)$ of this three-component system follows readily from Eq. (2.15) and the definition of the structural susceptibility. Here $\varphi_A=\varphi_1+\varphi_2$ and $\varphi_B=1-\varphi_A$ are the volume fractions of bonds A and B, $x=N_2/N_1\ll 1$, and $y=\varphi_2/\varphi_1\ll 1$ is the fraction of the low-molecular component A_{N_2}. In (6.1) we have discarded terms containing the small parameters x and y, but have retained the parameter

$$z=xyD_2/D_1\lambda_1=y/x\lambda(P_1, \mu_1), \tag{6.2}$$

which in general is not small. For $z\ll 1$ the contribution from A_{N_2} is negligible. Recalling the definition (3.6) of the self-diffusion coefficient, we can rewrite the opposite inequality $z\gg 1$ as

$$y\gg x\lambda(P_1, \mu_1), \tag{6.3}$$

which is similar to (5.19). In this case also, the impurity has little influence on the relaxation for times that are not too short, i.e., for t such that $w(t)$ is determined by those values of the Laplace transform variable p for which

$$P_1 \ll \mu_1 \lambda (P_1, \mu_1)/xy. \tag{6.4}$$

By contrast, for high frequencies $p \gg q^2 D_2$ expression (6.1) yields the contribution from the high-molecular component A_{N_1}, whose physical interpretation is obvious—for the very shortest times $t \gtrsim 0$, the density of the B polymer relaxes due to interdiffusion with the more mobile component A_{N_2} of the A polymer. The most interesting new effect caused by the impurity is that the relaxation function saturates:

$$w(t) = \frac{(\varphi_2 N_2)^{-1}}{(\varphi_2 N_2)^{-1} + (\varphi_B N_B)^{-1} - 2\chi}, \quad \frac{\varphi_2 N_2}{\varphi_B N_B q^2 D_B} \ll t \ll \frac{xy}{q^2 D_1 \lambda_1}, \tag{6.5}$$

if condition (5.19) is satisfied. However, it should be stressed that these new "impurity" asymptotics are always present for small enough times and have little effect on the results in Sec. 5. It follows from inequality (6.4) that the rather unrestrictive condition

$$\max\{|\tilde{\chi}|, (\mu^2 + \mu^{-1})\} \ll (xy)^{-1} \tag{6.6}$$

suffices for all of the regimes described there to be observable.

The consequences of finite compressibility can be analyzed as in the above discussion of impurity effects. We need only note that allowing for a nonzero φ in the direct susceptibility matrix (2.11a) for an n-component system is equivalent to considering an $(n + 1)$-component incompressible system in which the $(n + 1)$th component consists of "holes," i.e., fictitious particles of infinite mobility whose number per unit volume is equal to φ / v. The finite compressibility can therefore modify only the high-frequency asymptotic of the relaxation function, in full accord with the principal physical result of Sec. 5—namely, that the interaction among the polymer bonds affects the short-time relaxation behavior (high frequencies), but the relaxation for large times is determined solely by the reptation mechanism specific to polymers.

CONCLUSIONS

We have shown that density relaxation in high-molecular melts has several distinctive features which are not present for low-molecular solutions and can be effectively analyzed in the microscopic approach due to I. M. Lifshitz. The generalization to other polymer relaxation processes is of considerable interest but lies beyond the scope of this paper.

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