# Dynamics of weakly-coupled linear macromolecules

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Results are presented of an investigation of low-frequency relaxation processes in concentrated solutions and melts of polymers—systems of weakly coupled linear macromolecules. The effectiveness of a single-molecule approximation is demonstrated in which it is assumed that each macromolecule moves among its neighbors as if in an after-acting medium. An approach is examined which is confirmed by studying phenomena of optical anisotropy, diffusion, and neutron scattering, and which leads to a theory of viscoelasticity of polymer systems that turns out to be self-consistent.

## INTRODUCTION

Polymers differ from other materials by the size of their molecules which, appropriately enough, are referred to as macromolecules, since they consist of thousands or tens of thousands of atoms (molecular weight up to 10<sup>6</sup> or more) and have a macroscopic rectified length (up to  $10^{-4}$  cm). The atoms of a macromolecule are firmly held together by valence bonds, forming a single entity. In polymeric materials, atoms in different macromolecules experience the weaker van der Waals forces, and at temperatures above the characteristic glass transition and crystallization points, the polymeric system can be looked upon as a weakly-coupled system of macromolecules (the system is then a concentrated solution or melt, i.e., a polymeric liquid). When the system is excited (mechanically or thermally), the macromolecules can readily change their neighbors, but the integrity of each individual macromolecule remains unaffected.

The structure of polymeric liquids is more complicated than that of polymeric solids or low-molecular liquids, but there are some common properties: the atoms within a given macromolecule are ordered, but the centers of mass of the individual macromolecules and parts of them are distributed randomly. Remarkably, the mechanical response of polymeric systems combines the elasticity of a solid with the fluidity of a liquid. Indeed, their behavior is described as viscoelastic.<sup>1</sup> This property is typical of slow (relaxation time up to 1 sec or more) relaxation processes that are commonly associated with the relaxation of an individual macromolecule in a system.<sup>2,3</sup> Different research groups have made valiant attempts during the last 20-30 years to find a unified approach to polymeric systems that would provide an explanation and description of nonequilibrium phenomena in polymers from a unified point of view. The history of these searches is instructive and has its share of moments of drama. Indeed, there have been quite a few unsuccessful hypotheses (which nevertheless helped to advance our understanding of the behavior of polymers), but we shall not concentrate our attention on history. Instead, we present a review and an analysis of the present state of the subject.

Our understanding of the situation as of the end of 1986 is summarized in the monograph by Doi and Edwards,<sup>3</sup> but intensive studies of the dynamic properties of polymers have continued, and we now have a much better picture of the behavior of entangled linear polymers. The theory of nonequilibrium phenomena in polymers cannot, however, be regarded as complete. Nevertheless, researchers appear to be on course toward a clear understanding of the thermal motion of macromolecules in concentrated polymeric systems, which provides a unified basis for the formulation of a theory of nonequilibrium phenomena in these systems.

## 1. LOW-FREQUENCY MODES OF THE THERMAL MOTION OF MACROMOLECULES

The structure of a polymeric system is such that the thermal motion of its component macromolecules is different from the thermal motion of atoms and molecules in liquids or solids. This is particularly clearly shown by the localization effect whereby the mean displacement is a monotonic but nonlinear function (cf. Section 1.5) and the macromolecule remains near its initial position.

We begin our discussion of macromolecular dynamics with a schematic picture of an individual macromolecule.

## 1.1. Gaussian subchains

The statistical theory of long chains developed in considerable detail in Refs. 4–6 defines the equilibrium variables that characterize a macromolecular coil as a whole, including the mean square end-to-end distance  $\langle R^2 \rangle_0$  and the mean square radius of inertia  $\langle S^2 \rangle_0$  as functions of the micromolecular parameters. Whatever its chemical composition, a long enough macromolecule will roll up into a coil as a result of thermal motion, so that its mean square radius of inertia becomes proportional to its molecular length M:

$$\langle R^2 \rangle_0 \sim M.$$

A macromolecule cannot always be described with the help of  $\langle R^2 \rangle_0$  or  $\langle S^2 \rangle_0$  alone. Very long macromolecules require the more detailed, more macroscopic, and more universal method introduced by the pioneering work reported in Refs. 7 and 8 whereby the macromolecule is divided into N subchains of length M/N each. The points at which the subchains join to form the macromolecule will be labeled 0 to N, respectively, and their positions will be represented by  $\mathbf{r}^0$ ,  $\mathbf{r}^1...\mathbf{r}^N$  (Fig. 1). If we assume that each subchain is also sufficiently long, and can be described in the same way as the entire chain, the equilibrium probability distribution for the positions of all the beads in the macromolecule is

FIG. 1. Universal schematization: whatever the chemical structure, the macromolecule is represented by a flexible filament (persistent length model) or chain of freely joined segments (Kuhns' model) or chain of Brownian particles (subchain model; the figure shows only two particles).

$$W(\mathbf{r}^{0}, \mathbf{r}^{1}, ..., \mathbf{r}^{N}) = C \exp(-\mu A_{\alpha \gamma} \mathbf{r}^{\alpha} \mathbf{r}^{\gamma}), \qquad (1.1)$$

where

$$\mu = 3/2b^2 = 3N/2\langle R^2 \rangle_0, \tag{1.2}$$

and the matrix A takes the form

$$\begin{vmatrix} 1 & -1 & 0 & \dots & 0 \\ -1 & 2 & -1 & \dots & 0 \\ 0 & -1 & 2 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \dots & 1 \end{vmatrix}$$
(1.3)

We note that the free energy of a macromolecule in this approach is given by

$$F(\mathbf{r}^0, \mathbf{r}^1, ..., \mathbf{r}^N) = \mu T A_{\alpha} \mathbf{r}^{\alpha} \mathbf{r}^{\gamma}$$

and this determines the force per site in the first order in r

$$K_i^{\nu} = -\frac{\partial F}{\partial r_i^{\nu}} = -2\mu T A_{\nu\nu} r_i^{\nu}$$
(1.4)

where  $\nu$  is the site number.

The Gaussian subchain model can be generalized in a number of ways. When additional flexibility has to be taken into account, we have to add the interaction between different sites, so that the matrix (1.3) is replaced, for example, by a five-diagonal matrix; it is possible to take into account the finite extension of subunits by including in (1.4) terms of higher order in r, and so on.

When the equilibrium and nonequilibrium characteristics of the macromolecular coil are calculated, this is conveniently done in terms of new coordinates, defined by

$$\mathbf{r}^{\beta} = Q_{\beta\alpha} \vec{\rho}^{\ast \alpha}, \ \vec{\rho}^{\ast \alpha} = Q_{\alpha\gamma}^{-1} \mathbf{r}^{\gamma} \tag{1.5}$$

and such that the quadratic form in (1.1) assumes a diagonal form, so that

$$Q_{\lambda\mu}A_{\lambda\gamma}Q_{\gamma\beta} = \lambda_{\mu}\delta_{\mu\beta}$$

We shall follow tradition and refer to the new variables as the normal coordinates.

It is readily seen that the determinant of the matrix given by (1.3) is zero, so that one of the eigenvalues, say,  $\lambda_0$  is always zero. The normal coordinate corresponding to the zeroth eigenvalue

$$\rho^0 = Q_{0\nu}^{-1} r^{\gamma},$$

is proportional to the position vector of the center of mass of the macromolecular coil

 $\mathbf{q} = \frac{1}{N+1} \sum_{\alpha=0}^{N} \mathbf{r}^{\alpha}.$ 

The behavior of a macromolecule is conveniently de-

scribed in a coordinate frame with origin at the center of mass of the system. There are then only N normal coordinates, numbered from 1 to N.

The distribution function (1.1), normalized to unity, then assumes the following form:

$$W(\vec{\rho}^{1}, \vec{\rho}^{2}, ..., \vec{\rho}^{N}) = \prod_{\gamma=1}^{N} \left(\frac{\mu\lambda_{\gamma}}{\pi}\right)^{3/2} \exp(-\mu\lambda_{\gamma}\vec{\rho}^{\gamma}\vec{\rho}^{\gamma}). \quad (1.6)$$

The transformation matrix Q can be chosen in a variety of ways. In particular, it can be orthogonal and normalized. For large N and small values of  $\alpha$ , the eigenvalues are then given by (cf., for example, Ref. 9)

$$\lambda_{\alpha} = (\pi \alpha / N)^2, \quad \alpha = 0, 1, 2, \dots \ll N.$$
(1.7)

In the case of an orthogonal transformation, the relationship between the normal coordinate corresponding to the zeroth eigenvalue and the position of the center of mass of the chain is

$$\vec{\rho}^{*0} = \frac{1}{(N+1)^{1/2}} \sum_{\alpha=1}^{N} r^{\alpha}.$$
 (1.8)

Because of its universal character, this model plays a fundamental part in the theory of equilibrium and nonequilibrium properties of polymers. When N = 1, the subchain model transforms into the simple model of a flexible macromolecule, i.e., a dumbbell with two beads connected by a spring. This model was introduced by the Kuhns<sup>10</sup> as a first step toward the dynamics of a macromolecule in a flow.

We note that the above results are valid for a free noninteracting massless chain that constitutes a very useful idealization. However, the monomers in a macromolecule interact with one another, and this ensures, above all, that parts of the molecule cannot occupy the volume already occupied by other parts; i.e., the probabilities of successive steps are no longer statistically independent, as was assumed in the derivation of the above probability distribution functions and mean end-toend distance. For this subchain model, the equilibrium distribution function that includes the particle interaction potential can be taken in the form

$$W = C \exp(-\mu A_{\alpha \gamma} r^{\alpha} r^{\gamma} - T^{-1} U), \qquad (1.9)$$

where C is the normalization constant and U is the lateral interaction energy, measured by the second virial coefficient<sup>11</sup> B. The inclusion of interaction leads to a change in the root mean square distance  $\langle R^2 \rangle$  as compared with the unperturbed dimensions characterizing the massless macromolecule,  $\langle R^2 \rangle_0 = Nb^2$ . When dimensional considerations are taken into account, this quantity can be written in the form

$$\langle R^2 \rangle = Nb^2 f(N, B/b^3).$$
 (1.10)

This turns out to be particularly significant when one investigates dilute polymer solutions whose behavior is discussed in Refs. 11–15.

#### 1.2. Macromolecule in a concentrated system

We now turn to the concentrated polymer solution or melt. We assume that the system contains n identical macromolecules per unit volume. The position of each macromolecule can be defined, as before, by specifying certain points along the macromolecule, spaced at distances that are equal, but not too small; as before, we shall refer to these points as particles. If we take N + 1 points to define the position of the macromolecule, we shall need 3n(N+1) coordinates to specify the state of the entire system. The state of the system is described by the distribution of all the particles, and the corresponding equilibrium function is

$$W = C \exp\left(-\mu \sum_{a} A_{\gamma\nu} r^{a\gamma} r^{a\nu} - \frac{U}{T}\right), \qquad (1.11)$$

where  $\mathbf{r}^{a\gamma}$  is the coordinate of the  $\gamma$ th bead of a macromolecule labeled *a* or, in short, the coordinate of the point  $a\gamma$ ;  $\mu$  and the matrix *A* are given by (1.2) and (1.3), respectively. The potential energy associated with the "lateral" interaction between the chains depends on the difference between the coordinates of all the particles in the system.

There is particular interest in the distribution function for a single macromolecule and in the mean dimensions of a macromolecular coil in the system.

In contrast to the case considered in Section 1.1 [see (1.10)], the root mean square end-to-end distance is now a function of three parameters

$$\langle R^2 \rangle = N b^2 f(N, B/b^3, nb^3), \qquad (1.12)$$

where b is the mean separation between neighboring particles in a chain and B is the second virial coefficient. The number of macromolecules is related to the concentration c of the polymer in solution:

$$n = 6,026 \cdot 10^{23} c/M \cdot cm^{-3}$$
.

In a dilute solution, the macromolecular coils exist independently of each other. The parameter  $nb^{3}$  in (1.12) then has a very slight effect. However, as the concentration of the polymer increases, the separation d between the coil centers decreases, and when

$$d = 2\langle S^2 \rangle^{1/2}, \tag{1.13}$$

where  $\langle S^2 \rangle$  is the mean square radius of gyration, the coils begin to overlap. This condition defines the critical molecular weight for a given concentration, or the critical concentration of the solution for a given molecular mass, for which overlap begins.



FIG. 2. Schematic diagram showing the mean size of a macromolecular coil as a function of the polymer concentration. The example is taken of a macromolecule in a good solvent, so that at low concentrations  $\langle R^2 \rangle / \langle R^2 \rangle_0 > 1$ . The curves illustrate two variants of this dependence.

Further increase in the the concentration of the polymer is accompanied by interpenetration of the coils. As shown in Refs. 16 and 17, the mean dimensions of the coils are then found to approach their unperturbed values, i.e., values they would have had in the  $\Theta$ -solvent (Fig. 2).

For concentrations approaching the limiting value  $(c \rightarrow 1)$ , the system of macromolecular coils becomes spatially homogenenous, and portions of different macromolecules are found at each point; i.e., the molecular coils become entangled. Volume interactions are then screened<sup>2</sup> and the coil becomes ideal; i.e., the coil dimensions in the concentrated system are the same as the dimensions of ideal coils. This is confirmed by direct measurements of the dimensions of macromolecular coils in concentrated solutions and melts (cf. Refs. 18 and 19). By integrating (1.11) with respect to the coordinates of the particles of all the macromolecules except the chosen one, we obtain

$$W = C \exp(-\mu A_{yy} \mathbf{r}^{y} \mathbf{r}^{y}), \qquad (1.14)$$

where, as before,  $\mu$  is given by (1.2).

The entanglement of macromolecular coils in a concentrated system leads to a specific topological interaction between macromolecules in the system, i.e., to the formation of sites and tangles. This interaction is particularly conspicuous in nonequilibrium phenomena.

Discussions of dynamic phenomena in polymers are frequently based on assumptions about the structure of the system, which is often taken to be a network with characteristic site lifetime and nearest-neighbor separation.<sup>19</sup> A modification of this is the theory that postulates a certain internal scale, such as the diameter of a tube in which macromolecular displacement, i.e., reptation, is possible, but this hypothetical internal scale has not been detected anywhere except in dynamic phenomena, and its existence should be a consequence rather than the starting point of the theory. The theory that we shall consider below does not rely on the assumption of an internal scale, but it does assume that the mean size  $\langle R^2 \rangle$  and the macromolecular number density *n* (or concentration *c*) are the most significant parameters of the system.

We shall not discuss here the spatial correlation functions introduced in Refs. 2 and 16 for a more detailed description of system dynamics, or the relative position of the monomeric branches, since they are relatively unimportant in our, admittedly very coarse, approximation.

## 1.3. Dynamics of a macromolecule in the monomolecular approximation

We shall consider the motion of a macromolecule when the above system is deformed with a constant velocity gradient tensor

$$v_{ij} = \frac{\partial v_i}{\partial x_j},$$

so that a particle located at  $r_j^{\alpha}$  is dragged with mean velocity  $v_{ij}r_j^{\alpha}$ , which leads to the stretching of the macromolecular coil as the system is deformed. We shall also use the following notation for the symmetrized and unsymmetrized velocity gradients, respectively:

$$\gamma_{ii} = (1/2)(\nu_{ii} + \nu_{ii}), \, \omega_{ii} = (1/2)(\nu_{ij} - \nu_{ji})$$

When we consider relatively slow motion of concentrated polymer solutions or melts, each macromolecule will be schematically described as consisting of N + 1 linearly coupled Brownian particles, so that we shall be able to look upon the system as a suspension of n(N + 1) interacting Brownian particles suspended in a viscous "monomeric liquid." The collective motion of the entire set of macromolecules is then described by a set of stochastic Markov equations which, for slow motion, can be written in the form

$$m\frac{\mathrm{d}^{2}r_{i}^{\alpha\alpha}}{\mathrm{d}t^{2}} = B_{\alpha\alpha,b\beta}(\dot{r}_{i}^{b\beta} - \nu_{ij}r_{j}^{b\beta}) - 2\mu T A_{\alpha\gamma}r_{i}^{\alpha\gamma} - \frac{\partial U}{\partial r_{i}^{\alpha\alpha}} + \phi_{i}^{\alpha\alpha}(t),$$
(1.15)

where  $P_i^{a\alpha}$  is the coordinate of the particle labeled  $\alpha$ , which belongs to a molecule labeled a, and m is the mass of a Brownian particle associated with a piece of the macromolecule of length M / N. The first term on the right is the hydrodynamic drag force, determined through the matrix  $B_{a\alpha,b\beta}$  by all the Brownian particles in the system. The second term represents the force due to nearest-neighbor Brownian particles along the chain, and the third term is the direct interaction between all the Brownian particles. The last term represents the random thermal force whose statistical properties are, as usual, defined so that the equilibrium values of the calculated quantities are the same as those already known. Intramolecular friction forces (internal viscosity and kinetic stiffness) that arise when the macromolecular coil is deformed<sup>13,14</sup> are omitted because they are small in comparison with other forces.

A force acting on any part of the system gives rise to the excitation of the entire ensemble of Brownian particles, so that when the behavior of the system and the mechanical forces are investigated we have to consider the collective motion of all the particles in the same way that, for example, we examine the motion of the ensemble of atoms in a solid. Our first task is therefore to find the normal coordinates of the polymer system, i.e., the variables that vary independently of one another.

The identification of the normal coordinates can be carried out in two stages, bearing in mind the particular properties of the system (strong interaction along the chain and weak interaction between the macromolecules). The task of the first stage is to determine the dynamics of a single macromolecule, surrounded by all the others. Evaluation of the mean characteristics is not the only way of taking the influence of the latter into account. The validity of the so-called monomolecular approximation rests essentially on the fundamental experimental fact that quantities that characterize the behavior of the polymer system have a well-defined singlevalued dependence on the length of the macromolecule. This is followed by the second stage in which the normal coordinates of an individual macromolecule are determined.

To implement the first stage, we must eliminate all variables, other than those that refer to the chosen macromolecule, from the set of stochastic equations given by (1.15). Judging by published results,<sup>20-22</sup> this procedure is not too simple, but the form of the final results can be written down before the calculations are carried out. The requirements of covariance and of linearity in coordinates and velocities, determine<sup>23</sup> the general form of the equation for the dynamics of the chosen molecule:

$$n\frac{\mathrm{d}^{2}r_{i}^{\alpha}}{\mathrm{d}t^{2}} = \int_{0}^{\infty} \beta(s)(\dot{r}_{i}^{\alpha} - \nu_{i}f_{j}^{\alpha})_{t-s}\mathrm{d}s - \int_{0}^{\infty} \varphi(s)(\dot{r}_{i}^{\alpha} - \omega_{ij}r_{j}^{\alpha})_{t-s}\mathrm{d}s - 2\mu T A_{\alpha\gamma}r_{i}^{\gamma} + \phi_{i}^{\alpha}(t).$$
(1.16)

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The fundamental property of this equation is the presence of resistance and drag forces, represented by the first and second terms with memory, as confirmed by the direct analysis of this problem.<sup>21</sup> Strictly speaking, we should also write down these terms in the form of nonlocal expressions, since excitation directly through the chain propagates to a distance  $\langle R^2 \rangle$ , i.e. a distance that is large in comparison with the size of the Brownian particle under consideration. However, for the sake of simplicity, this will not be done here, although the consequences of a nonlocal effect will be noted latter. Equation (1.6) also relies on the questionable assumption that each particle in the chain is in the same isotropic situation. The third term on the right of (1.16) represents elastic forces on each Brownian particle due to its neighbors along the particle chain, which ensure the integrity of the macromolecule. These forces are assumed to be the same as in dilute solutions, but 'lateral' interactions are not taken into account for the reasons mentioned in the last Section.

Equation (1.16) is the most general equation for the dynamics of an individual macromolecule in the case of a linear dependence on coordinates and velocities. However, the memory functions  $\beta(s)$  and  $\varphi(s)$  cannot be determined from general considerations: they must be found by calculations such as, for example, those reported in Ref. 2, or simple model considerations must be abandoned as was done in Refs. 24 and 25 (we shall return to this later).

The first term in (1.16) represents the resistance-drag force experienced by a particle when the system is deformed:

$$F_i^{\alpha} = -\int_0^{\infty} \beta(s)(\dot{r}_i^{\alpha} - v_{ij}r_j^{\alpha})_{t-s} \mathrm{d}s. \qquad (1.17)$$

Each Brownian particle in a chain, except for the first and the last, which are unimportant for long chains, can be looked upon as a particle in a cell consisting of flexible elastic rods (Fig. 3) immersed in a monomeric liquid. The resistance experienced by a moving particle can then be divided into two terms, namely, the resistance due to the liquid, represented by a coefficient  $\zeta$ , and the viscoelastic reaction of the rods, due to the entanglement of the ambient macromolecules. In the simple case of a single relaxation time,

$$\beta(s) = 2\zeta\delta(s) + (\zeta/\tau)Be^{-s/\tau}$$
(1.18)

where we have introduced the relaxation time of the ambient medium which, as we shall see later (cf. Section 2.2) is the characteristic relaxation time of a molecular coil. This suggests that the theory is self-consistent and the coefficient B is a measure of the increase in the friction coefficient due to the fact that, for slow motion, the particle leaves behind a wake of ambient macromolecules. When this effect is taken into account, and the environment (a concentrated solution of the polymer) is looked upon as a nonlocal liquid, it is found<sup>26</sup> that, for a small Brownian particle, the coefficient B increases with increasing length of the macromolecules surrounding the chosen macromolecule:

$$B \sim M^{\delta}, \quad \delta > 2. \tag{1.19}$$



FIG. 3. Bead in a cell: the motion of the bead is resisted by the 'monomeric' liquid and the viscoelastic reaction of the 'cell' walls.

For sufficiently long chains,  $B \ge 1$ . The estimate obtained for the exponent is therefore very approximate and must be improved.

The second term in (1.16) represents the intramolecular resistance due to the change in the shape of the macromolecular coil. In contrast to the dilute solution, here this effect is due to the entanglement of the macromolecules and to the resistance due to the motion of the particles relative to one another (Fig. 4). The resistance force can be written in a form that is linear in the coordinates and velocities:

$$G_i^{\prime} = -\int_0^{\infty} \varphi(s)(\dot{r}_i^{\prime} - \omega_{ik}r_k^{\prime})_{t-s} \mathrm{d}s, \qquad (1.20)$$

where

$$\varphi(s) = (\zeta/\tau) E e^{-s/\tau}.$$
 (1.21)

The relaxation times that appear in the memory functions given by (1.18) and (1.21) are equal because they are both determined by the macromolecules in the environment.

The above equation is a generalization of the equation for the dynamics of the macromolecule in a dilute solution: the effective viscosity of the liquid in which the Brownian particle moves has been replaced in the case of the concentrated solution with an effective viscoelastic liquid, which brings in the concept of microviscoelasticity. Of course, if the relaxation times in (1.18) and (1.21) are short in comparison with the characteristic relaxation time of the macromolecule, then (1.16) becomes identical with the equation of motion of the macromolecule in a viscous liquid, which was used in Ref. 15 to describe the dynamics of dilute polymer solutions.



FIG. 4. The mechanism of 'intramolecular friction': relative motion of points  $\alpha$  and  $\beta$  on a given macromolecule is accompanied by the deformation of chain  $\Gamma$ , which gives rise to additional energy dissipation.

In terms of normal coordinates, to which we transform in accordance with the rule defined by (1.5), the set of equations for the Brownian particles, given by (1.16), now assumes the form

$$m\frac{d^{2}\rho_{i}^{\nu}}{dt^{2}} = -\int_{0}^{\infty}\beta(s)(\dot{\rho}_{i}^{\nu} - \nu_{ij}\rho_{j}^{\nu})_{t-s}ds - \int_{0}^{\infty}\varphi(s)(\dot{\rho}_{i}^{\nu} - \omega_{ij}\rho_{j}^{\nu})_{t-s}ds - 2T\mu\lambda_{\nu}\rho_{i}^{\nu} + Q_{\alpha\nu}\phi_{i}^{\alpha}(t).$$
(1.22)

The eigenvalues  $\lambda_{\nu}$  are given by (1.7). Equation (1.22) should also contain a description of the static properties of the stochastic force, defined so that  $\langle \phi_i^a(t) \rangle = 0$ . The second-order moment

$$K_{ij}^{\alpha\gamma}(t, t') = Q_{\nu\alpha} Q_{\beta\gamma} \langle \phi_i^{\nu}(t) \phi_j^{\beta}(t') \rangle$$
(1.23)

depends on velocity gradients and can be expanded into a series in powers of this quantity. The first-order term cannot in general satisfy the conditions of symmetry under the interchange of the arguments of the function (1.23), and must therefore be discarded. This means that, to within first-order terms in velocity gradients, the correlation function has the same form as in the equilibrium, i.e., time-independent, case:

$$K_{ij}^{\alpha\gamma}(t, t') = K_{\alpha}(t - t')\delta_{\alpha\gamma}\delta_{ij}.$$

The random force correlator is determined by demanding that, in equilibrium, the moments of velocities and coordinates must be known. In our simple case, the Fourier transform of the correlator does not depend on the mode number:

$$K(\omega) = \int_{-\infty}^{\infty} K(s)e^{i\omega s} = 2T \operatorname{Re} B[\omega], \qquad (1.24)$$

where the one-sided Fourier transform of a function is indicated by brackets:

$$B[\omega] = \beta[\omega] + \varphi[\omega]. \tag{1.25}$$

For functions defined by (1.18) and (1.21), we have

$$\beta[\omega] = \zeta \left( 1 + \frac{B}{1 - i\omega\tau} \right),$$
(1.26)
$$\varphi[\omega] = \frac{\zeta E}{1 - i\omega\tau}.$$

Equation (1.22) and the definition of the stochastic force can be looked upon as the first-order approximation (linearity in coordinates and velocities and in velocity gradients) to nonequilibrium phenomena in dilute polymers. This excludes effects due to nonlinear terms, e.g., the reptation phenomena noted by de Gennes,<sup>27</sup> which appear when the difference between mobilities along and at right angles to the chain is taken into account. This can be described by terms of order greater than the first in a rigorous theory of motion of a macromolecule in a concentrated system. However, before we turn to this problem, we must examine the effects represented by linear terms.

The set of equations given by (1.22), which will be presented later in a different form in (1.53), determines the lowfrequency modes of the thermal motion of a system of weaklyinteracting macromolecules for v = 1, 2, ....

## 1.4. Correlation functions and relaxation times

The average size and shape of a macromolecular coil in a deformable system are described by the correlation moments

$$\langle \varphi_i^{\alpha} \varphi_k^{\alpha} \rangle = \int W(\rho) \varphi_i^{\alpha} \varphi_k^{\alpha} \{ d\rho \}.$$

It is readily shown using (1.6) that, in equilibrium, these moments take the form

$$\langle \varphi_i^a \varphi_k^a \rangle_0 = (1/2\mu\lambda_a) \delta_{ik}. \tag{1.27}$$

A macromolecule will on average form a spherically symmetric coil in both dilute and concentrated solutions. Deformation of the system produces a change in the shape and size of macromolecular coils.

To calculate these moments, we start<sup>23</sup> with (1.22), which is conveniently written in the form

$$\rho_{i}^{\alpha}(t) = \int_{0}^{\infty} [\chi_{\alpha}(s)Q_{\gamma\alpha}\phi_{i}^{\gamma}(t-s) + (\mu_{\alpha}(s)\nu_{il}(t-s) + \pi_{\alpha}(s)\omega_{il}(t-s))\rho_{l}^{\alpha}(t-s)]ds,$$
(1.28)

where the functions  $\chi_a$ ,  $\mu_a$ , and  $\pi_a$  are determined by their Fourier transforms

$$\chi_{\alpha}[\omega] = (2T\mu\lambda_{\alpha} - m\omega^{2} - i\omega B[\omega])^{-1},$$
  

$$\mu_{\alpha}[\omega] = \beta[\omega]\chi_{\alpha}[\omega], \ \pi_{\alpha}[\omega] = \varphi[\omega]\chi_{\alpha}[\omega]$$
(1.29)

and vanish for  $s \rightarrow 0$  and  $s \rightarrow \infty$ .

Differentiating (1.28) with respect to time, and integrating by parts, we find, using the properties of the integrands, that

$$\dot{\rho}_{i}^{\alpha}(t) = \int_{0}^{\infty} [\dot{\chi}_{\alpha}(s)Q_{\gamma\alpha}\phi_{i}^{\gamma}(t-s)ds + (\dot{\mu}_{\alpha}(s)\nu_{il}(t-s) + \dot{\pi}_{\alpha}(s)\omega_{il}(t-s))\rho_{l}^{\alpha}(t-s)]ds.$$
(1.30)

Iteration of (1.28) and (1.30) can be used to expand the normal coordinates and velocities of Brownian particles into series in powers of small velocity gradients of the medium and then, by multiplying and averaging, to obtain the expression for any grouping. The moments of coordinates and velocities evaluated in this way<sup>23</sup> are written out below:

$$\langle \varphi_i^{\alpha}(t) \varphi_k^{\alpha}(t) \rangle = M_{\alpha}(0) + 2 \int_0^{\infty} \mu_{\alpha}(s) M_{\alpha}(s) \gamma_{ik}(t-s) ds, \langle \dot{\varphi}_i^{\alpha}(t) \dot{\varphi}_k^{\alpha}(t) \rangle = \frac{T}{m} \delta_{ik} + 2 \int_0^{\infty} \dot{\mu}_{\alpha}(s) \dot{M}_{\alpha}(s) \gamma_{ik}(t-s) ds,$$
 (1.31)  
 
$$\langle \varphi_i^{\alpha}(t) \dot{\varphi}_k^{\alpha}(t) \rangle = M_{\alpha}(0) \omega_{ki}(t)$$

$$+ \int_{0}^{\infty} \left[ \mu_{\alpha}(s) \dot{M}_{\alpha}(s) + \dot{\mu}_{\alpha}(s) M_{\alpha}(s) \right] \gamma_{ik}(t-s) \mathrm{d}s,$$

$$\langle \varphi_i^{\alpha}(t)\varphi_k^{\alpha}(t-s)\rangle = M_{\alpha}(s)\omega_{ki}(t-s)$$
  
+ 
$$\int_0^{\infty} \left[ \dot{\mu}_{\alpha}(u)M_{\alpha}(s+u) + \mu_{\alpha}(s+u)\dot{M}_{\alpha}(u) \right]\gamma_{ik}(t-s-u)du.$$

These moments are given to within terms of the first order in velocity gradients. A different procedure, described in Section 1.6, has to be used to evaluate the second and higher order terms.

The functions  $\mu_{\alpha}(s)$  and  $M_{\alpha}(s)$  and their derivatives must be known before we can evaluate the moments (1.31). The one-sided Fourier transform of the function  $\mu_{\alpha}(s)$  is given by (1.29). The other function is defined as the coordinate correlation function

$$M_{a}(s)\delta_{ik} = \langle \rho_{i}^{a}(t)\rho_{k}^{a}(t-s) \rangle$$
(1.32)

with (1.27) taken at s = 0. The expression for the one-sided Fourier transform is found from (1.28) and (1.30), using the fluctuation-dissipation relation given by (1.24). It takes the form

$$M_{\alpha}[\omega] = \frac{1}{2\mu\lambda_{\alpha}} \frac{B[\omega] - im\omega}{2T\mu\lambda_{\alpha} - m\omega^2 - i\omega B[\omega]}.$$
 (1.33)

This expression is valid for an arbitrary function  $B[\omega]$ , but to reconstruct the correlation function, we start with (1.26), derived in the last Section for a simple model. In the present model, inertial forces acting on the Brownian particles are then unimportant, so that we can neglect the mass, but the final expressions will contain the following function of a nonnegative argument:

$$E(t) = \lim_{m \to 0} e^{-\zeta t/m} = \begin{cases} 1 & t = 0, \\ 0 & t > 0, \end{cases}$$
(1.34)

 $\dot{E}(t)=-2\delta(t).$ 

If we carry out these calculations for

$$B[\omega] = \zeta \left( 1 + \frac{B+E}{1-i\omega\tau} \right)$$

in the absence of inertia (m = 0), we obtain<sup>28</sup>

$$M_{\alpha}(t) = \frac{1}{2\mu\lambda_{\alpha}} \frac{1}{\tau_{\alpha}^{+} - \tau_{\alpha}^{-}} (S_{\alpha}^{+} e^{-t/2\tau_{\alpha}^{+}} - S_{\alpha}^{-} e^{-t/2\tau_{\alpha}^{-}}),$$
  

$$\mu_{\alpha}(t) = \frac{1}{\tau_{\alpha}^{+} - \tau_{\alpha}^{-}} (T_{\alpha}^{+} e^{-t/2\tau_{\alpha}^{+}} - T_{\alpha}^{-} e^{-t/2\tau_{\alpha}^{-}}),$$
  

$$T_{\alpha}^{\pm} = (1 + B)\tau^{R} - \tau^{\mp}, \quad S^{\pm} = (1 + B + E)\tau^{R} - \tau^{\mp}.$$
  
(1.35)

These expressions contain the two relaxation times  $\tau_a^+$ and  $\tau_a^-$  of the macromolecular coil. They are given by

$$2\tau_{\alpha}^{\pm} = \tau_{\alpha} \pm (\tau_{\alpha}^{2} - 2\tau\tau_{\alpha}^{R})^{1/2}, \qquad (1.36)$$
$$\tau_{\alpha} = \frac{\tau}{2} + (1 + B + E)\tau_{\alpha}^{R},$$

where  $\tau_{\alpha}^{R} = \tau^{*}/\alpha^{2}$  represents the Rouse relaxation times, i.e., the relaxation times of the macromolecule in the viscous liquid.

The relaxation times are now determined not only by the Rouse relaxation time, but also by a further three parameters, namely, the relaxation time  $\tau$  of the medium, which acts as an

initiating parameter for the relaxation process, the measure B of the increase in the particle friction coefficient due to the wake behind the particle when it moves slowly among the chains, and the internal viscosity E associated with the resistance to deformation of the coil due to its entanglement by ambient macromolecules. All three parameters increase with increasing length of ambient macromolecules.

It is also interesting to consider the simpler case in which  $\zeta$  can be neglected in comparison with  $\zeta B$  and  $\zeta E$ . However, an incorrect result is obtained by going to the limit in (1.33): it is essential to maintain the order in which the limit is approached. We first take  $m \rightarrow 0$  and only then  $\zeta \rightarrow 0$ . The result is

$$M_{\alpha}(t) = \frac{1}{2\mu\lambda_{\alpha}} [(B+E)\frac{\tau_{\alpha}^{R}}{\tau_{\alpha}}e^{-t/2\tau_{\alpha}} + \frac{\tau}{2\tau_{\alpha}}E(t)],$$

$$\mu_{\alpha}(t) = B\frac{\tau_{\alpha}^{R}}{\tau_{\alpha}}(e^{-t/2\tau_{\alpha}} - E(t)).$$
(1.37)

These expressions can be used with (1.31) to calculate any moments in which we are interested. For example, we can show that, after a perturbation, the single-time moments of the coordinates approach  $(m = 0, \zeta = 0, \zeta B \neq 0)$  their equilibrium value in accordance with

$$\langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle = (1/2\mu\lambda_{\alpha})\delta_{ik} + \Delta_{ik}^{\alpha} e^{-i/\tau_{\alpha}}.$$
 (1.38)

We note that, in simple cases, the optical anisotropy of polymeric systems is directly related<sup>28</sup> to differences between the moments of coordinates,  $\langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle - \langle \rho_i^{\alpha} \rho_k^{\alpha} \rangle_0$ , so that bire-fringence experiments can reveal the relaxation of moments and can yield estimates of the relaxation times. Analysis of this situation<sup>28</sup> shows that there is good agreement between measured and theoretical relaxation laws.

#### 1.5. Mobility of macromolecules

There are significant differences between the thermal motion of a macromolecule in a dilute solution and a macromolecule in a melt (amongst other macromolecules). In the former case, the macromolecule moves as a Brownian particle in a viscous liquid, and its displacement is given by the standard expression

$$\langle \Delta q^2 \rangle = 6D_0 t \tag{1.39}$$

where  $D_0$  is the coefficient of diffusion, which is inversely proportional to the mobility of the macromolecular coil. For a molecule in a flowing liquid without volume effects

$$D_0 \sim T/M$$

Let us now consider the thermal motion of a macromolecule constrained by other macromolecules.<sup>25</sup> We shall calculate the mobility of a macromolecule in thermodynamic equilibrium in which there are no velocity gradients and viscosity-type forces do not arise, so that we can start with the equation of dynamics, i.e., (1.16), without the second term on the right-hand side, and use the expressions for the moments obtained earlier.

We shall calculate the root mean square displacement of the center of mass of a diffusing macromolecule in a time t, using the expression

$$\langle \Delta q^2 \rangle = \int_0^t \int_0^t \langle \dot{q}(s) \dot{q}(u) \rangle ds du. \qquad (1.40)$$

This reduces to the evaluation of the time-domain velocity correlation function

$$\langle \dot{\varphi}_i^0(s) \dot{\varphi}_k^0(u) \rangle = (1 + N) \langle \dot{q}_i(s) \dot{q}_k(u) \rangle.$$

We now turn to the expression for this function given by (1.31), and consider the simple case without inertia for which

$$B[\omega] = \zeta + \frac{\zeta B}{1 + i\omega\tau}.$$

.. ..

We then find that the displacement of the center of mass of a macromolecule is

$$\langle \Delta q^2 \rangle = \frac{6T\tau}{\zeta NB} \left( \frac{t}{\tau} + 1 - e^{-tB/\tau} \right). \tag{1.41}$$

Figure 5 shows the displacement as a function of the ratio  $t/\tau$  for B = 100.

For short times of observation,  $t \ll \tau/B$ , the expression for the displacement takes the form

$$\langle \Delta q^2 \rangle = (6T/N\zeta)t$$

and is identical with (1.39) which was written for the displacement of a macromolecule in a flowing viscous liquid. The constraints due to the other macromolecules then become insignificant, and the expression for the diffusion coefficient of a macromolecule in a flow is the same as for the corresponding monomeric viscous liquid:

$$D_0 = T/N\zeta.$$

The mobility of the macromolecule falls sharply for  $t = \tau/B$ , but the displacement remains constant over a certain time of observation, and is given by

. .

$$\langle \Delta \mathbf{q}^2 \rangle = \frac{6T\tau}{N\zeta B} = \frac{\langle R^2 \rangle_0 \tau}{\pi^2 \tau^* B} = \frac{2}{\pi^2} \langle R^2 \rangle_0 \chi = \xi^2. \tag{1.42}$$

The characteristic time  $\tau/B$  is thus associated in the theory with a characteristic scale; i.e., we have a localization effect. The dimensionless quantity  $\chi$  can be interpreted as the ratio of the square of twice the characteristic scale to the root mean square end-to-end distance of the macromolecule:

$$\chi = \frac{\tau}{2B\tau^*} = \frac{\pi^2}{8} \frac{(2\xi)^2}{\langle R^2 \rangle_0} \approx \frac{(2\xi)^2}{\langle R^2 \rangle_0}.$$
 (1.43)



FIG. 5. The displacement of the center of mass of a macromolecule, calculated from (1.41), demonstrates the existence of the localization scale  $\xi$ .

The quantity  $\xi$  may be expected to be a characteristic of the system of chains, and is independent of the length M of the macromolecules forming the system, so that

$$\chi \sim M^{-1}$$

The situation is different for long observation times  $t \ge \tau$ . Constraints by neighboring macromolecules then play a significant part, and (1.41) gives the expression for the displacement:

$$\langle \Delta \mathbf{q} \rangle = (6T/N\zeta B)t.$$

Hence it follows that, in this particular situation, the motion of a test chain is also coupled to the motion of neighboring macromolecules, and the diffusion coefficient is determined both by the length M of the test macromolecule and by the length of the ambient macromolecules:

$$D \sim M_0^{-2} M^{-1}. \tag{1.44}$$

The diffusion coefficient for long chains is small, and we then encounter a competing mobility mechanism that gives a different dependence of the diffusion coefficient on the length of the macromolecule. It is important to remember that a particle that is part of a macromolecule surrounded by other macromolecules exhibits anisotropic mobility; i.e., the motion of a bead along the molecule is easier than motion in the perpendicular direction. This can be taken into account by introducing an anisotropic mobility or, more coarsely, by introducing a tube of finite diameter  $2\xi$  [ $\xi$  is defined by (1.42) ] formed by the surrounding macromolecules, so that the only possible motion is motion along the tube, i.e., reptation.<sup>27</sup> The diffusion coefficient of the macromolecule does not then depend on the length of the ambient macromolecules<sup>27</sup>

$$D \sim M_0^0 M^{-2}. \tag{1.45}$$

Thus, for long observation times, we have two competing mechanisms for the displacement of a macromolecule with diffusion coefficients given by (1.44) and (1.45). By studying the mobility of a macromolecule of length M among chemically similar but shorter macromolecules of length  $M_0$ , we can differentiate between these mechanisms because they have a different length dependence of the self-diffusion coefficient:

$$D \sim M^{-3}, \quad D \sim M^{-2}.$$
 (1.46)

Of course, when the macromolecules are long enough, the reptation mechanism predominates, and this has indeed been confirmed experimentally.<sup>29</sup>

We note once again that reptation is a nonlinear effect. To describe it, we must add nonlinear terms to the equation of motion (1.16). These are in effect added in Ref. 27 by introducing the tube. However, it would be wrong to conclude in the light of existing experiments that the concept of molecular reptation can provide a description of relaxation phenomena, including viscoelasticity. Actually, to construct first-order theory, it is sufficient to confine our attention to terms in the equation of motion for the macromolecule that are linear in coordinates and velocities.

A detailed analysis of particle displacement in a chain is given in Ref. 30 for observation times  $t \ll \tau/B$  for which the displacements of chain particles are small, small-scale motion of the beads confined to the scale  $\xi$  can take place (chain in a *tube*), and large scale chain conformation is frozen. For long times of observation, the particle mobility is reduced, but displacement is unrestricted, and higher-order effects that were not examined in the theory become possible, e.g., sliding in a tube, as discussed by de Gennes.<sup>27</sup> This picture of motion is confirmed by studies of quasielastic neutron scattering by specially prepared samples.<sup>31</sup>

#### 1.6. Relaxation equations

When the dynamic equations were formulated and the moments were evaluated, this was subject to the condition that the relationships used were valid to within terms of the first order in velocity gradients. On the other hand, when the moments are calculated in the higher-order approximations based on the model of a macromolecule moving in a medium consisting of all the other macromolecules, we must also allow for the fact that deformation of the medium makes it anisotropic because each Brownian particle moves in an anisotropic viscoelastic liquid. This was neglected when the analysis was confined to linear effects.

The amplification coefficients B and E in the dynamic equations [cf. formulas (1.18) and (1.21)] will now be written as tensor quantities that depend on the tensor

$$a_{ij} = (\langle S_i S_j \rangle / \langle S^2 \rangle) - (1/3)\delta_{ij}$$

where the gyration tensor of the macromolecular coil is given by

$$\langle S_i S_j \rangle = \frac{1}{N+1} \sum_{\alpha=1}^n \langle \varphi_i^{\alpha} \varphi_j^{\alpha} \rangle.$$

In the linear approximation,

$$B_{ij} = B[\delta_{ij} - 3\beta(a_{ij} - \frac{1}{3}a_{ll}\delta_{ij}) - \varkappa a_{ll}\delta_{ij}],$$

$$E_{ij} = E[\delta_{ij} - 3\varepsilon(a_{ij} - \frac{1}{3}a_{ll}\delta_{ij}) - \varkappa a_{ll}\delta_{ij}].$$
(1.47)

To calculate the moments, it is convenient to write down the dynamic equations (1.16) for a macromolecule in the form proposed in Ref. 32.

The external resistance force given by (1.17) in accordance with the function (1.18) can be split into two terms, one of which is constant and equal to  $\zeta(\dot{r}_j^{\gamma} - v_{jl}r_l^{\gamma})$ , and the other satisfies the equation

$$r\left(\frac{dF_i^{\alpha}}{dt} - \omega_{il}F_l^{\alpha}\right) + F_i^{\alpha} = -\zeta B_{ij}(\dot{r}_j^{\alpha} - \nu_{jl}r_l^{\alpha}).$$
(1.48)

Similarly, the internal resistance (1.20) can be taken in the form

$$\tau \left( \frac{\mathrm{d}G_i^{\alpha}}{\mathrm{d}t} - \omega_{il}G_l^{\alpha} \right) + G_i^{\alpha} = -\zeta E_{ij}(\dot{r}_j^{\alpha} - \omega_{jl}r_l^{\alpha}). \tag{1.49}$$

It is readily verified that, in the linear approximation, these relations are given by (1.17) and (1.20), whereas in the nonlinear approximation, equations (1.48) and (1.49) give the expressions for the forces that are covariant under timedependent transformations. We note that more detailed information about the covariance principle for relaxation phenomena can be found in Ref. 33 (page 13).

As before, it is convenient to transform to normal coordi-

nates. Taking the forces in terms of the new variables

$$\Gamma_i^{\alpha} = Q_{\gamma\alpha} F_i^{\gamma}, \quad T_i^{\alpha} = Q_{\gamma\alpha} G_i^{\gamma}, \tag{1.50}$$

we can rewrite (1.22) in terms of the newly defined forces (1.48) and (1.49) in the form

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\rho_{i}^{\alpha} &= \psi_{i}^{\alpha}, \\ m\frac{\mathrm{d}}{\mathrm{d}t}\psi_{i}^{\alpha} &= -\zeta(\psi_{i}^{\alpha} - \nu_{ij}\rho_{j}^{\alpha}) + \Gamma_{i}^{\alpha} + T_{i}^{\alpha} - 2T\mu\lambda_{\alpha}\rho_{i}^{\alpha} + Q_{\gamma\alpha}\phi_{i}^{\gamma}, \\ \tau\left(\frac{\mathrm{d}}{\mathrm{d}t}\Gamma_{i}^{\alpha} - \omega_{il}\Gamma_{l}^{\alpha}\right) + \Gamma_{i}^{\alpha} &= -\zeta B_{ij}(\psi_{j}^{\alpha} - \nu_{jl}\rho_{l}^{\alpha}), \\ \tau\left(\frac{\mathrm{d}}{\mathrm{d}t}T_{i}^{\alpha} - \omega_{il}T_{l}^{\alpha}\right) + T_{i}^{\alpha} &= -\zeta E_{ij}(\psi_{j}^{\alpha} - \omega_{jj}\rho_{l}^{\alpha}). \end{aligned}$$
(1.51)

These stochastic forces are determined by the corresponding correlation functions which, as usual,<sup>34</sup> are found from the requirement that, in equilibrium, the set of equations given by (1.51) must lead to well-known results. This condition determines the random-force correlation function

$$K_{ij}^{\alpha\mu}(t, t') = Q_{\gamma\alpha}Q_{\beta\mu}\langle \phi_i^{\gamma}(t)\phi_j^{\beta}(t')\rangle = K_{ij}(t-t')\delta_{\alpha\mu},$$

where, by virtue of (1.24), we have

$$K_{ij}(s) = 2T\zeta\delta(s) + (T\zeta/\tau)(B_{ij} + E_{ij})e^{-s/\tau}.$$
 (1.52)

Next, following Ref. 32. we introduce the new variable  $\varphi_i^{\alpha}$  (the acceleration) and, eliminating the variables  $\Gamma_i^{\alpha}$  and  $T_i^{\alpha}$  from (1.51), we write down the dynamic equations in the following form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_i^{\alpha} = \psi_i^{\alpha}, \quad \frac{\mathrm{d}\psi_i^{\alpha}}{\mathrm{d}t} = \varphi_i^{\alpha}, \tag{1.53}$$

$$m\left[\tau\left(\frac{\mathrm{d}}{\mathrm{d}t}\varphi_{i}^{\alpha}-\omega_{il}\varphi_{l}^{\alpha}\right)+\varphi_{l}^{\alpha}\right]+2T\mu\lambda_{\alpha}\left[\tau(\psi_{i}^{\alpha}-\omega_{il}\rho_{l}^{\alpha})+\rho_{i}^{\alpha}\right]$$
$$+\zeta B_{ij}(\psi_{j}^{\alpha}-\nu_{il}\rho_{l}^{\alpha})+\zeta E_{ij}(\psi_{j}^{\alpha}-\omega_{jl}\rho_{l}^{\alpha})$$
$$+\zeta\left[\tau(\varphi_{i}^{\alpha}-\omega_{il}\psi_{l}^{\alpha})+\psi_{i}^{\alpha}\right]$$
$$-\tau(\nu_{ii}\psi_{i}^{\alpha}-\omega_{il}\nu_{li}\rho_{i}^{\alpha})-\nu_{ii}\rho_{i}^{\alpha}]=\xi_{i}^{\alpha}.$$

These are stochastic equations with a random force that is related to the above random forces by

$$\xi_{i}^{\alpha} = Q_{\gamma\alpha} \left[ \phi_{i}^{\gamma} + \tau \left( \frac{\mathrm{d}}{\mathrm{d}i} \phi_{i}^{\gamma} - \omega_{il} \phi_{l}^{\gamma} \right) \right], \qquad (1.54)$$

which can be looked upon as the equation for the random quantity  $\varphi_i^{\gamma}$  for given random  $\xi_i^{\alpha}$ . It is readily seen that, if the relation

$$\langle \xi_i^{\alpha}(t)\xi_j^{\mu}(t')\rangle = 2T\zeta(B_{ij} + E_{ij})\delta_{\alpha\mu}\delta(t-t'), \qquad (1.55)$$

is satisfied, the random-force correlator satisfies the following relation by virtue of (1.54):

$$K_{ii}(s) = (T\zeta/\tau)(B_{ii} + E_{ii})e^{-s/\tau}.$$

The quantity (1.52) differs from the above expression only by the presence of the first term, so that, if  $\zeta = 0, \zeta B \neq 0, \zeta E \neq 0$ , the random source in (1.53) becomes  $\delta$ -correlated. However we cannot proceed to this limit immediately, since we are interested, in the final analysis, in the results obtained for m/ζ≪τ,

i.e., we must first pass to the limit m = 0.

The set of stochastic equations given by (1.53) is equivalent (in the linear case) to (1.16) with the memory functions defined in Section 1.3 but, in contrast to the latter case, (1.53)is written as a set of Markov stochastic equations. This enables us to determine the variables that describe the collective motion of the set of macromolecules. In this particular approximation, the interaction between neighboring macromolecules ensures that the phase variables of the elementary motion are the position coordinate, the velocity, and the acceleration. The set of elementary modes describes the dynamics of the entire set of entangled and weakly-interacting macromolecules.

We can now use (1.53) without any fundamental difficulty to find the equations for any moment, e.g., for

$$x_{ij}^{\alpha} = \langle \rho_i^{\alpha} \rho_j^{\alpha} \rangle, \quad y_{ij}^{\alpha} = \langle \rho_i^{\alpha} \psi_j^{\alpha} \rangle.$$

For example, in the above case  $(m = 0, \zeta = 0, \zeta B \neq 0, \zeta E \neq 0)$ , it can be shown that, to within terms of the first order in the small nonlinearity coefficients  $\beta = x$  and  $\varepsilon = v$ , the relaxation equation is<sup>35</sup>

$$\begin{aligned} \frac{\mathrm{d}x_{ik}^{\alpha}}{\mathrm{d}t} &- \omega_{ij} x_{jk}^{\alpha} - \omega_{kj} x_{ji}^{\alpha} = -\frac{1}{\tau_{\alpha}} (x_{ik}^{\alpha} - \dot{x}_{ik}^{\alpha}) + B \frac{\tau_{\alpha}^{R}}{\tau_{\alpha}} (\gamma_{il} \chi_{lk}^{\alpha} + \gamma_{kl} x_{li}^{\alpha}) \\ &- 3B \frac{\tau_{\alpha}^{R}}{\tau_{\alpha}} \left( \beta - (\beta + \psi \varepsilon) B \frac{\tau_{\alpha}^{R}}{\tau_{\alpha}} \right) (a_{il} \gamma_{lj} x_{jk} + a_{kl} \gamma_{lj} x_{ji}) \\ &+ 3B \frac{\tau_{\alpha}^{R}}{\tau_{\alpha}} (\beta + \psi \varepsilon) \frac{1}{2\tau_{\alpha}} [a_{ij} (x_{jk}^{\alpha} - x_{jk}^{\alpha}) + a_{kj} (x_{ji}^{\alpha} - x_{ji}^{\alpha})], \end{aligned}$$

$$(1.56)$$

where the relaxation time is given by (1.36).

In the time-independent case, the solution of the relaxation equation given by (1.56) can be readily found in the form of an expansion in powers of velocity gradients. If we confine our attention to terms of the second order in velocity gradients, we obtain

$$\begin{aligned} x_{ik}^{\alpha} &= \frac{1}{2\mu\lambda_{\alpha}} \{\delta_{ik} + 2B\tau_{\alpha}^{R}\gamma_{ik} + 2B\tau_{\alpha}^{R}\tau_{\alpha}(\omega_{il}\gamma_{lk} + \omega_{kl}\gamma_{li}) \\ &+ 4(B\tau_{\alpha}^{R})^{2}\gamma_{il}\gamma_{lk} - \frac{4\pi^{2}}{15}B^{2}\tau^{*}\tau_{\alpha}^{R} \bigg[\beta - 2(\beta + \psi\varepsilon)\frac{B\tau_{\alpha}^{R}}{\tau_{\alpha}}\bigg]\gamma_{il}\gamma_{lk}\}. \end{aligned}$$

$$(1.57)$$

The first terms in this expression are, naturally, identical with the expression obtained in the corresponding approximation in Section 1.4.

#### 2. THE VISCOELASTICITY OF CONCENTRATED POLYMERS

When we described macromolecular dynamics, we assumed that the environment could be characterized by a delayed reaction, i.e., by viscoelasticity. We are now in a position to calculate the mean stresses in the system and to determine the parameters of the viscoelastic behavior. We find that the relaxation time of the environment found in Section 1, is equal to the relaxation time of the entire system, which we have already calculated. The theory is thus seen to have the necessary self-consistency without requiring any additional conditions or assumptions.

#### 2.1. Stresses under deformation

A very concentrated polymer solution or melt is a system of entangled chains that we investigate on the basis of the monomolecular approximation; i.e., we consider that the system can be represented by a set of noninteracting macromolecules whose behavior is described with allowance for their environment. Each macromolecule is schematically represented by a chain of N + 1 Brownian particles, so that the system may be looked upon as a suspension of Brownian particles but, in contrast to the dilute solution, these particles are suspended in a viscoelastic liquid. The set of Brownian particles can be characterized, as in the case of the dilute solution, by mean density

$$\rho(\mathbf{x}, t) = \sum_{\alpha} m \langle \delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle = m(N+1)n(\mathbf{x}, t)$$
(2.1)

and mean momentum density

$$\rho(\mathbf{x}, t)\mathbf{v}(\mathbf{x}, t) = \sum_{\alpha} m \langle \dot{\mathbf{r}}^{\alpha} \delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle.$$
(2.2)

The angle brackets represent averaging over the ensemble of realization of random forces in the particle equations of motion. The sum in (2.1) and (2.2) is evaluated over all the Brownian particles.

When the equations of motion are formulated, which is equivalent to the derivation of the expression for the stress tensor,<sup>33</sup> we have to take into account the presence of the two interacting and interpenetrating continuous media formed by the viscoelastic liquid carrier and the interacting Brownian particles that model the macromolecules.

However, the contribution of the carrier in the case of the concentrated solution is slight, and we shall ignore it henceforth.

We shall use standard procedure<sup>36</sup> to find the stress tensor. We start with the definition of the momentum density, given by (2.2), which is valid for an arbitrary set of Brownian particles. Differentiating (2.2) with respect to time, and using the equation of motion given by (1.16), we find the equation for the mean momentum density of the Brownian particles:

$$\frac{\partial}{\partial t}\rho v_{k} = \sum_{\alpha} \langle K_{k}^{\alpha} \delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle$$
$$- m \frac{\partial}{\partial x_{i}} \sum_{\alpha} \langle \dot{r}_{i}^{\alpha} \dot{r}_{k}^{\alpha} \delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle - \sum_{\alpha} \langle G_{k} \delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle + R_{k},$$
(2.3)

where the elastic force  $K_k^{\alpha}$  and the intramolecular friction force  $G_k$  are given by (1.4) and (1.20), repectively. In (2.3), we have separated out the mean drag acting on the Brownian particles:

$$R_{k} = -\sum_{\alpha} \int_{0}^{\infty} \langle \beta(s)(\dot{r}_{k}^{\alpha} - v_{kl}r_{l}^{\alpha})_{l-s}\delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle \mathrm{d}s$$
$$+ \sum_{\alpha} \langle \phi_{k}^{\alpha}(t)\delta(\mathbf{x} - \mathbf{r}^{\alpha}) \rangle.$$

Next, we use the formal expansion of the  $\delta$ -function into

a Taylor series around the center of mass  $q^a$  of the *a*th macromolecule, and retain only the first two expansion terms:

$$\delta(\mathbf{x} - \mathbf{r}^{\alpha}) = \delta(\mathbf{x} - \mathbf{q}^{\alpha}) - (r_{j}^{\alpha} - q_{j}^{\alpha}) \frac{\partial}{\partial x_{j}} \delta(\mathbf{x} - \mathbf{q}^{\alpha}).$$

Substituting this expansion into the right-hand side of (2.3), we obtain an equation that has the form of the equation of motion and determines the mean stress. Assuming that all the macromolecules are identical, and neglecting the statistical dependence of the position of the centers of mass of the macromolecules on the other coordinates, we write the stress tensor in the form

$$\sigma_{ik} = -n \sum_{\alpha} \left[ m \langle (\dot{r}_i^{\alpha} - v_i) (\dot{r}_k^{\alpha} - v_k) \rangle + \langle K_i^{\alpha} r_k^{\alpha} + G_i^{\alpha} r_{k'}^{\alpha} \right], \quad (2.4)$$

where n is the macromolecular number density. In (2.4), the sum is evaluated over the particles in a given macromolecule.

Recalling the expression for the forces K and G, and assuming that the particle velocities are described by the local equilibrium distribution, we write the stress tensor in the following form in terms of normal coordinates:

$$\sigma_{ik}(t) = -nT\delta_{ik} + nT\sum_{\alpha=1}^{N} \{2\mu\lambda_{\alpha}\langle \varphi_{i}^{\alpha}(t)\varphi_{k}^{\alpha}(t)\rangle - \delta_{ik} + \frac{1}{T}\int_{0}^{\infty} \varphi(s) [\langle \varphi_{i}^{\alpha}(t)\dot{\varphi}_{k}^{\alpha}(t-s)\rangle - \omega_{kl}(t-s)\langle \varphi_{l}^{\alpha}(t-s)\varphi_{i}^{\alpha}(t)\rangle] ds \}.$$

$$(2.5)$$

This expression can also be written in the symmetrized form<sup>35</sup> and determines the stress tensor in terms of the correlation functions of coordinates and velocities of the beads, obtained in Section 1.4. The monomolecular approximation ensures that the stress tensor of the system is the sum of the contributions of all the macromolecules.

We note that, if  $\varphi(s)$  is independent of time  $(\tau \rightarrow 0)$ , the expression for the stress tensor, given by (2.5), reduces to

$$\sigma_{ik} = -nT\delta_{ik} + n\sum_{\alpha=1}^{N} [2\mu T\lambda_{\alpha} \langle \rho_{i}^{\alpha} \rho_{k}^{\alpha} \rangle - T\delta_{ik} + \varphi(\langle \dot{\rho}_{k}^{\alpha} \rho_{i}^{\alpha} \rangle - \omega_{k} \langle \rho_{l}^{\alpha} \rho_{i}^{\alpha} \rangle)].$$
(2.6)

If we use the moments for the macromolecular coil in a viscous liquid in this expression, the result is identical with the expression for the stress tensor in a dilute polymer solution in the theory of Cerf<sup>37</sup> and Peterlin.<sup>38</sup> In this approach, internal viscosity is taken into account in the linearized variant.

#### 2.2. Dynamic modulus and relaxation times

Polymer systems have appreciable elasticity. Initially,<sup>19</sup> this elasticity was ascribed to the presence of a network in the system formed by long macromolecules with junction sites. The expression for the modulus of elasticity was written by analogy with the theory of elasticity of linear polymers:<sup>4</sup>

$$G'_e = nTM/M_e, \tag{2.7}$$

where  $M_e$  is the length of a macromolecule between neighboring sites.

Attempts to describe the viscoelastic behavior of the

polymer system in terms of sites and nets were unsuccessful, although the concept of an internal scale has survived and has been used to write down a formula analogous to (2.7).

The viscoelastic behavior of the polymer system can be seen with particular clarity by imposing a one-directional oscillatory motion

$$\gamma_{ik} \sim e^{-i\omega t}$$

The expression for the stresses, given by (2.5), then assumes the form

$$\sigma_{ik}(t) = -p\delta_{ik} + 2\eta(\omega)\gamma_{ik}(t)$$

and determines the complex viscosity  $\eta = \eta' - i\eta'$ . It is also convenient to describe the system in terms of the dynamic modulus which is related to the dynamic viscosity by

$$G(\omega) = G'(\omega) - iG''(\omega) = -i\omega\eta(\omega).$$

Later in this Section, we shall examine the dependence of the dynamic modulus of concentrated polymer solutions as a function of frequency, polymer concentration, and molecular weight. These functions have been the subject of extensive experimental investigation.<sup>19</sup> For example, Fig. 6 shows<sup>39</sup> the dynamic modulus of polystyrene. This is a typical graph for a linear polymer of high molecular mass and narrow molecularweight distribution.

To calculate the dynamic modulus, we turn to the expression given by (2.5)

To begin with, consider the case of low frequencies, so that  $\zeta$  can be neglected in comparison with  $\zeta B$  in (1.26). The moments (1.31) can then be determined with the help of (1.37), so that after some rearrangement we obtain



FIG. 6. Experimental and theoretical values of the real (a) and imaginary (b) components of the dynamic shear as functions of frequency. The points are taken from Ref. 39 for polystyrene with molecular weight 215000 at T = 160 °C. The theoretical values of the shear modulus and its components (dashed curve) were calculated by Yu. K. Kokorin for B = 3000, E = 20000,  $\chi = 0.08$ ,  $\tau^* = 5 \times 10^{-5}$  s,  $nT = 1.7 \times 10^{5}$  dyne/cm<sup>2</sup>.

$$G(\omega) = nT \sum_{\alpha} \left(\frac{\tau_{\alpha}^{R}}{\tau_{\alpha}}\right)^{2} B\left(B\frac{-i\omega\tau_{\alpha}}{1-i\omega\tau_{\alpha}} + E\frac{\tau_{\alpha}}{\tau}\frac{-i\omega\tau_{\alpha}^{0}}{1-i\omega\tau_{\alpha}^{0}}\right). \quad (2.8)$$

Thus, at low frequencies, the viscoelastic behavior of the system is determined by two sets of relaxation times

$$\tau_{\alpha} = \frac{\tau}{2} + (B + E)\tau_{\alpha}^{R}, \quad \tau_{\alpha}^{0} = \frac{2\tau\tau_{\alpha}}{2\tau_{\alpha} + \tau}, \quad \tau_{\alpha}^{R} = \frac{\tau^{*}}{\alpha^{2}}, \quad (2.9)$$

in which for small  $\alpha$  and the above large B we have

$$\tau_a \gg \tau_a^0, \quad \tau_a^0 \approx \tau$$

The dynamic modulus of the system is determined by two relaxation branches and is a function of frequency and of the above dimensionless parameters

$$G(\omega) = G(\omega\tau^*, B, \chi, \psi). \tag{2.10}$$

Figure 7 shows the measured modulus<sup>40</sup> and the theoretical results based on (2.8) in the low-frequency region. The individual terms in (2.8) are also shown separately for the two relaxation modes. This demonstrates that the principal contribution to the modulus is due to the branch with relaxation time  $\tau_{\alpha}^{0}$ . The contribution of the first term in (2.8), which is due to ultraslow relaxation processes, was practically unnoticable for most of the systems that were investigated: the first term had a slight effect on the imaginary part of the modulus and a small knee appeared on the real part.

To analyze these results, consider the asymptotic behavior of (2.8). The modulus reaches a plateau at high frequencies:

$$G_{\mathbf{e}}' = \lim G(\omega),$$

whereas, at low frequencies, the expansion

$$G(\omega) = -i\omega\eta - \omega^2\nu \tag{2.11}$$



FIG. 7. Experimental and theoretical values of the dynamic shear modulus as a function of frequency. The points are taken from Ref. 40 for hydrogenized polybutadiene with molecular weight of 215 000 at 130 °C. The theoretical values of the modulus and of its two components (dashed and marked 1 and 2 in the figure) were calculated by Yu. K. Kokorin from (2.8) for  $\chi = 0.0056$ ,  $\psi = 7.5$ , and  $B \ge 1$ .

determines the viscosity  $\eta$  and the elasticity  $\nu$ . Equation (2.11) can then be used to determine the elasticity for very low frequencies  $\nu_{\infty}$  and intermediate values of  $\nu$ .

We now need estimates of the parameters  $\chi$  and  $\psi$  before we can proceed. A preliminary estimate of  $\chi$  which, according to (1.43), can be interpreted as the ratio of the square of the tube diameter  $(2\xi)^2$  to the mean square end-to-end distance  $\langle R^2 \rangle_0$ , shows that  $\chi \ll 1$  for arbitrary  $\psi$  and sufficiently long macromolecules. For large N, this enables us to replace summation by integration and to obtain expressions for the characteristic quantities:

$$G'_{e} = nT \left[ \frac{\pi^{2}}{12} \frac{\psi}{\chi(1+\psi)} + \frac{\pi}{8} \frac{2-\psi}{\chi(1+\psi)^{3/2}} \right],$$
  

$$\eta = nT\tau^{*}B \left[ \frac{\pi^{2}}{6} - \frac{\pi}{2} \left( \frac{\chi}{1+\psi} \right)^{1/2} \right],$$
  

$$v = nT(\tau^{*}B)^{2} \left[ \frac{\pi^{2}}{3} \frac{\chi\psi}{1+\psi} - \pi\psi \left( \frac{2\chi}{1+\psi} \right)^{3/2} \right],$$
  

$$v_{\infty} = v + \frac{\pi^{4}}{90} nT(\tau^{*}B)^{2}.$$
  
(2.12)

These expressions are valid for arbitrary  $\psi$  and small  $\chi$ . We can then distinguish between two cases, namely, for systems consisting of very long molecules we have  $\psi \ge 1$  in the almost complete absence of the solvent, whereas  $\psi \le 1$  for concentrated easily flowing polymers.

When  $\psi \ge 1$ , the following simple formulas follow from (2.12):

$$G'_{e} = \frac{\pi^{2}}{12} nT \chi^{-1} \qquad \eta = \frac{\pi^{2}}{6} nT \tau^{*} B$$

$$\nu = \frac{\pi^{2}}{3} nT (\tau^{*} B)^{2} \chi \qquad \nu_{\infty} = \frac{\pi^{4}}{90} nT (\tau^{*} B)^{2}.$$
(2.13)

We note that, in this particular case, i.e., for  $\chi \leq 1, \psi \geq 1$ , the main contribution to the modulus is provided by the second relaxation branch with relaxation times  $\tau_{\alpha}^{0}$ : the ratio of the second to first terms in the definition given by (2.8) for  $\omega \to \infty$  is equal to  $\psi^{2}\chi^{-1}$ , so that the experimental detection<sup>40</sup> of ultraslow relaxation processes—the first relaxation branch—was quite sensational. The relaxation times on the second branch are very close, so that the dependence of the modulus on frequency could be approximated by a relation with the single relaxation time

$$\frac{\eta}{G_{\rm e}'} = 2\tau^* B \chi = \tau$$

The relaxation time that we have determined may be referred to as the principal viscoeleastic relaxation time; it is equal to the relaxation time that was introduced to characterize the medium surrounding the chosen macromolecule; i.e., for  $\psi \ge 1$  the theory is self-consistent. This fact was noted in Ref. 23.

We note, recalling the previously mentioned interpretation of  $\chi$  as the ratio of the characteristic scale to the size of the coil [formula (1.45)], that the expression for the modulus on the plateau can be written in the form

$$G_{\rm e}' = (2/3)nT \langle R^2 \rangle_0 / (2\xi)^2. \tag{2.14}$$

Comparing the expression that we have obtained with (2.7), we note that the length  $M_e$  between the links, determined in the usual way, is actually related to the characteristic scale  $2\xi$ . Although a network is not present in a concentrated solution, there is a characteristic length, which had earlier been assumed to be the distance between neighboring network sites. The characteristic length (tube diameter)  $2\xi$  or length  $M_e$  between chain joints can be estimated from the modulus with the aid of the above formulas. A summary of the estimated characteristic lengths is given in Ref. 41.

To extend the theory to higher frequencies, we have to consider the general case where the microviscoelasticity is given by (1.26). If we use (1.31) and (1.35), we find that, in this case, the dynamic modulus is also a function such as (2.10) and is determined by five relaxation branches. Figure 6 shows the calculated and measured dynamic shear modulus of polystyrene together with the contributions due to the relaxation branches for values of  $\chi$  and B chosen so as to ensure agreement with the modulus on the plateau and the length of the plateau. Good agreement is achieved at high and low frequencies.

The slowest of the relaxation branches (ultraslow relaxation) is then practically absent from these plots. The second branch with relaxation time  $\tau$  is the significant one. The remaining branches merge together and form a group of slow relaxation times, so that two groups are usually noted,<sup>1</sup> namely, slow and fast. This picture is typical for concentrated polymer solutions and melts.

#### 2.3. Viscoelasticity of dilute polymer mixtures

By studying a mixture of two polymers, one of which is present in much smaller amounts, we have a unique opportunity to obtain direct information about the dynamics of a chosen isolated macromolecule in a viscoelastic liquid consisting of the matrix macromolecules.<sup>24</sup>

Consider a linear polymer with macromolecular weight  $M_0$  and a small impurity of a similar polymer with high molecular weight M. We assume that the amount of the high-molecular impurity is so small that its molecules do not interact with each other, so that the medium in which the molecules propagate is a system consisting of the linear polymer with molecular weight  $M_0$ , which is characterized by the modulus  $G_0(\omega) = -i\omega\eta_0(\omega)$ .

The change in stress produced by the small amount of macromolecules of another kind is, clearly, determined by the dynamics of the noninteracting impurity macromolecules among the macromolecules of another length, so that this case is of particular interest from the standpoint of the theory of viscoelasticty of linear polymers.

We now turn to the case of low frequencies for which the dynamic modulus can be written in the form of the expansion given by (2.11). We begin by considering the characteristic quantities

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{c\eta_0}, \quad [\nu] = \lim_{c \to 0} \frac{\nu - \nu_0}{c\nu_0}$$
(2.15)

as functions of the length (or the molecular weight) of the macromolecules of the matrix and the impurity. The index 0 refers to the matrix and c is the impurity concentration.

The viscoelastic behavior of dilute polymer mixtures was investigated experimentally in Refs. 42 and 43. The values of

 $[\eta]$  and  $[\nu]$  were found in Ref. 24 for mixtures of polybutadienes of different length and narrow molecular-weight distributions

$$[\eta] \sim M_0^{-0.8} M^{0.5},$$

$$[\nu] \sim M_0^{-(1,8+2,2)} M^{1,3+3,0}.$$
(2.16)

Following Ref. 24, we can calculate the characteristic quantities from the formulas given in the last Section. For the above mixtures of polymers, we must consider B, E, and  $\tau$  as functions of  $M_0$ , and  $\tau^*$  as a function of M, so that we now have

$$\chi = \tau / 2\tau^* B \sim M_0 M^{-2}. \tag{2.17}$$

The quantity  $\chi$  is again small, which ensures that the formulas given by (2.13) are valid and we find from them that

$$[\eta] = \frac{\pi^2}{6} \frac{nT\tau^*B}{c\eta_0}, \quad [\nu] = \frac{\pi^2}{3} \frac{nT(\tau^*B)^2 \chi}{c\nu_0}.$$
 (2.18)

We assume that the length of the macromolecules in the matrix is such that the discussion and results of the last Section apply to them, so that

$$\eta_0 = (\pi^2/6) n_0 T \tau_0^* B, \quad v_0 = (\pi^2/3) n_0 T (\tau_0^* B)^2 \chi_0,$$

where  $n_0$  is the number of macromolecules per unit volume and  $\tau_0^*$  is the characteristic relaxation time of the macromolecules of the matrix, where  $\tau_0^* \sim M_0^2$ .

Using the above relations, and recalling that  $n \sim c/M$ , we find that

$$[\eta] \sim M_0^{-1}M, \quad [\nu] \sim M_0^{-1}M. \tag{2.19}$$

These results do not depend upon the dependence of B on the length (molecular weight) of the macromolecule, which we have already estimated [see equation (1.19)].

We note that by considering the competing mechanism of thermal motion—the reptation of the macromolecules we obtain<sup>44</sup> the characteristic viscosity of the mixture:

$$[\eta] \sim M_0^{-3} M^3. \tag{2.20}$$

Comparison of the theoretical formulas (2.19) and (2.20) with experimental data shows that the experimental indices are closer to those in (2.19) than to those in (2.20). This comparison confirms that, in so far as the influence of the chosen macromolecule is concerned, the ambient macromolecules are equivalent to a certain viscoelastic medium, and shows that the reptation model is unsuitable for the description of relaxation processes. As already noted, the reason for this is that the reptation effect is due to terms of order higher than the first in the equation of motion of the macromolecule, and it is actually the first-order terms that dominate the relaxation phenomena. Attempts to describe viscoelasticity without the leading linear terms lead to a distorted picture, so that one begins to understand the lack of success of the reptation model in the description of the viscoelasticity of polymers. Reptations are found when one considers nonlinear effects in viscoelasticity.

The above results are valid for  $M \ge M_0$ . This is so because we have ignored the fact some of the macromolecules of the matrix were replaced by impurity macromolecules.

Actually, the system that contains  $n_0$  matrix macromolecules per unit volume and *n* impurity macromolecules per unit volume can be characterized by assuming the additivity of the change in the characteristic quanitites

$$\eta - \eta_0 = \frac{\pi^2}{6} n T \tau^* B \left( 1 - \frac{M_0}{M} \right),$$
  
$$\nu - \nu_0 = \frac{\pi^2}{3} n T (\tau^* B)^2 \chi \left( 1 - \frac{M_0}{M} \right).$$

When  $M \ge M_0$ , the above expressions reduce to (2.13), and the expression for the characteristic quantities assumes the form of (2.18). On the other hand, when  $M \ll M_0$ , the characteristic quanities are negative and are independent of the lengths of the matrix and impurity macromolecules

$$[\eta] \sim M_0^0 M^0, \quad [\nu] \sim M_0^0 M^0. \tag{2.21}$$

# 2.4. Dependence on the concentration, temperature, and length of macromolecules

Thus, in the monomolecular approximation or, in other words, in the mean-field approximation, the dynamic shear modulus of the melt or the concentrated solution of the polymer (2.10) is represented by a function of a small number of parameters whose significance was discussed in the previous Sections.

In the limiting case of concentrated solutions and melts of high-molecular polymers, we assume that  $B \ge 1$ . Hence it follows that  $\tau > \tau^*$ , which imposes certain restrictions on  $\chi$ , so that  $1/2B < \chi \leqslant 1$ . For these values of B and  $\chi$ , the theory is found to be self-consistent for  $\psi \ge 1$ , so that once again, as was shown in Section 2.2, the formulas for the dynamic modulus lead to the expressions for the characteristic quantities:

$$\eta = \frac{\pi^2}{6} n T \tau^* B, \quad \tau = \frac{\tau^*}{2B\chi}, \quad \nu = \frac{\pi^2}{3} n T (\tau^* B)^2 \chi, \quad (2.22)$$
$$G'_e = \frac{\pi^2}{12} n T \chi^{-1}.$$

The significance of the dynamic modulus and of the characteristic variables as functions of the polymer concentrations c and the length M of the macromolecule can be examined experimentally. The quantities B and  $\chi$  as functions of c and M at high concentrations can be written as functions of a single argument. Actually, since the above kinetic restrictions on the motion of a macromolecule are related to the geometry of the system, the only parameters in this case are the number of macromolecules per unit volume and the mean square end-to-end distance

$$\langle R^2 \rangle_0 \sim M.$$

The dimensionless quantities B and  $\chi$  are therefore universal and independent of the chemical structure of the polymers when expressed as functions of the dimensionless parameter

$$Z = n \langle R^2 \rangle_0^{3/2} \sim c M^{1/2}. \tag{2.23}$$

To determine the form of the functions  $\chi(Z)$  and B(Z), we turn to the data obtained for almost monodisperse samples of polymer melts of different molecular weight. Since experimental data<sup>19,45</sup> show that for high molecular weights  $\eta \sim M^{\delta + 1}$ ,  $G'_e \sim M^0$ , where, as a rule  $\delta = 2.4$ , it follows from (2.22) that

$$B \sim Z^{2\delta}, \chi \sim Z^{-2}$$

where  $\tau^* \sim M^2$ .

Theoretical estimates [cf. (1.19)] show that  $\delta = 2$ . The parameter *E*, which does not appear in (2.22), can also be represented by a power function whose exponent estimated from the relaxation time of ultraslow processes as function of the molecular weight<sup>43</sup> is the same as the exponent in the expression for *B*:

 $E \sim Z^{2\delta}$ .

Using the above expressions together with (2.22), we obtain the following functions of concentration and molecular mass (length) of a macromolecule:

$$\eta \sim \zeta c^{2\delta+1} M^{\delta+1}, \quad \nu \sim \zeta c^{4\delta-1} M^{2\delta+2},$$
(2.24)  
$$G'_{e} \sim T c^{3} M^{0}, \quad \tau \sim \frac{\zeta}{T} c^{2\delta-2} M^{\delta+1}.$$

These formulas establish the relationships between functions of the characteristic quantities. For example, in accordance with experimental data,<sup>19</sup> the dependence of  $\eta$  and of  $\tau$ on the length of a macromolecule is the same. The behavior of the initial viscosity is the most widely studied: the measured functions<sup>45-47</sup> are close to the theoretical results given by (2.24).

We note once again that the above discussion and expressions are valid only for very long macromolecules and in the limit of very high concentrations. For semidilute solutions, the analysis should also include a further dimensionless parameter (cf. Section 1.2), but then the results become more complicated. In particular, the expressions for the parameters B and E appear to be different because E/B tends to zero on dilution.

The temperature dependence of the characteristic quantities in (2.24) requires separate examination.

The friction coefficient  $\zeta$  in (2.24) is a function of temperature, concentration, and (for small M) of molecular weight:

 $\zeta = \zeta(T, \, c, \, M).$ 

The coefficient of friction is due to the motion of small portions of the macromolecule, so that its temperature dependence is similar to that found for low-molecular liquids, and can be written in the following form<sup>45</sup> at temperatures much higher than the glass point:

$$\zeta \sim e^{U/T},\tag{2.25}$$

where U is the activation energy that depends on molecular weight (for small M), concentration, and also temperature if the temperature range in which viscosity is considered is large. Near the glass point  $T_g$ , we have<sup>45</sup>

$$\zeta \sim \exp \frac{A}{f_g - \alpha_1 (T - T_g)}, \qquad (2.26)$$

where A is an individual parameter,  $f_g$  is the volume fraction of free volume, and  $\alpha_1$  is the expansion coefficient of the liquid. The quantities A and  $f_g$  are practically independent of concentration and molecular weight, so that the dependence of  $\zeta$  on c and M is determined by the dependence of  $T_g$  on these quantities. We note that, since the parameters B, E, and  $\chi$  are practically independent of temperature, the shape of the curves showing G/nT as a function of the frequency  $\tau^*\omega$  does not change with increasing temperature, so that we can have superposition with the reduction coefficient obtained from the temperature dependence of viscosity in accordance with the rule

$$G(a_T \omega, T_0) = (\rho(T_0) T_0 / \rho(T) T) G(\omega, T), \qquad (2.27)$$

where the reduction coefficient is given by

$$a_T = (T_0/T)(\eta(T)/\eta(T_0))(\rho(T_0)/\rho(T))^{2\beta+1}.$$
 (2.28)

The above expressions define a method of reducing the dynamic moduli measured at different temperatures to an arbitrarily chosen standard temperature  $T_0$ . We note that (2.28) offers a relatively insignificant improvement on the usual expression.<sup>39</sup>

#### 2.5. Nonlinear effects during flow

Irreversible flow of the system becomes appreciable for times of observation longer than the relaxation times of the system, the longest of which is, according to (2.9),  $\tau_1 = \tau(1 + \chi + \psi)/2\chi$ . Since  $\chi \ll 1$ , we find that for  $\psi \ll 1$ , the time  $\tau_1$  exceeds the principal relaxation time  $\tau$  by one or two orders of magnitude, whereas for  $\psi \gg 1$  it increases by several orders of magnitude. Since the observation time t is usually associated with the relatively long principal relaxation time  $\tau$ , the system does not exhibit appreciable reversible deformations for  $\psi \gg 1$ , whereas for  $\psi \ll 1$  it flows readily.

Flowing polymer liquids exhibit nonlinear effects, a review of which can be found in Ref. 19.

The flow conditions in viscometers are close to simple shear, specified by a constant velocity gradient tensor

$$\boldsymbol{\nu}_{ij} = \begin{bmatrix} 0 & \nu_{12} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

which is why simple shear flow is often used to demonstrate the properties of the rheological model, i.e., well-established relations between stresses and kinematic parameters.

When the local stresses that are necessary for the implementation of shear flow are calculated from (2.5), only the following shear stresses are nonzero in the first approximation in the velocity gradient:

$$\sigma_{12}^0 = \eta_0 \nu_{12}, \tag{2.29}$$

$$\eta_0 = (\pi^2/6)nTB\tau^*.$$

Higher-order approximations show that normal stresses are also necessary for the implementation of shear flow. For small values of the parameters  $\chi$ ,  $\psi$ ,  $\beta$ , it can be shown<sup>35</sup> that

$$\begin{aligned} \sigma_{12} &= \eta v_{12}, \\ \eta &= \eta_0 \left[ 1 + \left( \frac{\sigma_{12}^0}{nT} \right)^2 \left( \frac{72}{315} \psi + \frac{72}{15\pi^2} \chi + \frac{2232}{2725} \beta \right) \right], \\ \sigma_{11} + p &= nT \left( \frac{\pi^4}{45} + \frac{\pi^2}{6} \chi - \frac{\pi^4}{90} \beta \right) (B\tau^* v_{12})^2, \end{aligned}$$
(2.30)  
$$\sigma_{22} + p &= nT \left( \frac{\pi^2}{6} \chi + \frac{\pi^4}{90} \beta \right) (B\tau^* v_{12})^2, \qquad \sigma_{33} + p = 0. \end{aligned}$$

Three considerations lead to nonlinear effects in shear, namely, effective kinetic stiffness of the macromolecules  $(\psi)$ , response lag of surroundings  $(\chi)$ , and effects associated with the change in dimensions and shape of the macromolecular coils  $(\beta)$ .

The expressions given by (2.30) lead to the following expressions for stresses during shear:

$$J_{11} - \sigma_{33} = \frac{1}{nT} \left( \frac{4}{5} + \frac{6}{\pi^2} \chi - \frac{4}{10} \beta \right) \sigma_{12}^2,$$

$$\frac{\sigma_{22} - \sigma_{33}}{\sigma_{11} - \sigma_{33}} = -\frac{15}{2\pi^2} \chi - \frac{1}{2} \beta.$$
(2.31)

These expressions are amenable to experimental verification. Data typical for concentrated polymer systems<sup>19</sup> show that the normal stress difference  $\sigma_{11} - \sigma_{33}$  is proportional to the square of the shear stresses for low velocity gradients. The second difference between normal stresses  $\sigma_{22} - \sigma_{33}$  is small in comparison with the first, which agrees with the above statement that  $\chi$  and  $\beta$  were small.

In contrast to viscous liquids, the instantaneous introduction of a given velocity gradient in a viscoelastic liquid does not immediately produce the corresponding stress: the latter is established in a time comparable with the relaxation time. Moreover, and typically for polymeric liquids, the establishment of both shear and normal stresses is not monotonic.<sup>48,49</sup> Our theory can be used<sup>50</sup> to describe these properties, and this is illustrated in Fig. 8.

It is useful to note that other types of flow exhibit a variety of nonlinear effects. In contrast to the coefficient of shear viscosity, which decreases with increasing applied stress, the theoretical longitudinal viscosity

 $\lambda = \sigma / v_{11}$ 

increases with with applied tensile stress, in complete accord with experimental data.<sup>51</sup> The simplest set of equations is obtained in the zero-order approximation in the parameters  $\chi$ and  $\psi$ . The material constants are then the individual charac-



FIG. 8. Measured<sup>48</sup> (points) and theoretical (curves) values of tangential stress as a function of shear strain for velocity gradients (in s<sup>-1</sup>) of 0.0182 (1), 0.0313 (2), 0.0627 (3), and 0.125 (4). The theoretical curves were calculated<sup>50</sup> for nT = 1270 dyne/cm<sup>2</sup>,  $\tau_0 = 27.5$ s<sup>-1</sup>,  $\chi = 0.11$ , and  $\psi = 0.12$ .

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teristics of the system, namely, the initial shear viscosity and the initial relaxation time, which depend on temperature, molecular weight of the polymer, and its concentration in the system. The set of equations formulated in this way is the simplest system that takes into account the behavior of concentrated polymer solutions and melts, namely, the gradient dependence of shear voscosity, the normal stresses that arise in shear flows, the evolution of stresses during deformation, the gradient dependence of longitudinal viscosity, and other effects, so that these equations can be looked upon as the basic set for the study of inhomogeneous time-dependent flows of linear polymers.

The statistical theory of flow of polymeric liquids is the result of considerable effort by researchers, and has taken a considerable amount of time to emerge. The question therefore arises as to whether these equations could not have been obtained in some other, simpler way? Actually, the first attempts at a description of the flow of polymeric liquids were phenomenological, but unsuccessful. In the end, the principles of the thermodynamics of irreversible processes were employed to formulate a set of equations<sup>55</sup> that could be compared with the macromolecular theory.

## CONCLUSION

The fundamentals of the above theory of relaxation processes in concentrated polymeric systems, which can be described as the first-order self-consistent theory, were first formulated<sup>23</sup> in 1978, and in a less complete form by another author<sup>56</sup> in 1983. Despite the skeptical response it had received from experimentalists, and the continuing research into this problem,<sup>24–26,28,30–32,35,52</sup> there is no evidence of any conflict between the large volume of experimental data that has now accumulated and the above theory. This may be interpreted as showing that the slow relaxation processes described by this theory do indeed correspond to processes actually observed in concentrated polymeric systems.

Relaxation processes in concentrated polymer systems are thus seen to present a simple picture: in the first approximation, the dynamics of the system can be described as the dynamics of the individual molecules moving amongst other molecules as if they were a medium with delayed response. The results of the theory can be applied to slow (low frequency) motions, and are found to be independent of the detailed structure of the macromolecular chain. In this sense, they are universal. The chemical character of the polymer appears via the parameters of the theory. At high frequencies, relaxation processes and the viscoelastic behavior of the chain structure are determined by the details of the interaction between the macromolecules and their neighbors. In the latter case, we have to start with a macromolecular model that is more detailed than the subchain model, and take account of the orientational correlation between neighboring chain segments. This has indeed been done by a number of workers.<sup>14</sup>

The above procedure for the determination of normal coordinates appears to be validated by the fact that each macromolecule is a special macrosystem that can be described by phenomenological parameters and represented by a chain of Brownian particles that are large in comparison with atomic scales, but small enough to take part in thermal motion. A Brownian particle is traditionally considered<sup>34</sup> to be moving in a certain continuous medium that in this case is considered to exhibit delayed response. The use of average characteristics

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does not spoil the essential picture of slow macromolecular motion because of the large dimensions of the relaxing parts of the macromolecule and the small fluctuations in the mean field in the system. Other considerations such as those involving correlations between particles in different macromolecules appear to be relatively insignificant at low frequencies. Nevertheless, the above presentation of macromolecular dynamics is hypothetical and is verifiable by comparison with experiment. A theoretical validation of the hypotheses would also be desirable, and so the urgent problem in the theory of relaxation phenomena in polymers is to implement the idea of reducing the 'extra' coordinates in the 'correct' multimacromolecular set of equations, possibly by following the example of Ref. 21. The question thus reduces to a complex technical problem with a known solution.

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