

# Low-frequency dynamics of dilute solutions of linear polymers

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**Abstract.** A review is presented of the results of the theory of relaxation of the macromolecule and of the dynamics of a dilute solution of polymers, with intramolecular interactions, hydrodynamic impermeability, and internal viscosity of the macromolecule taken into account. The linear viscoelasticity and optical anisotropy of the system are examined. Typical features of the behaviour of dilute solutions of polymers at various frequencies are discussed.

## 1. Introduction

A dilute solution of a polymer is understood as a system of macromolecules in a solvent such that the macromolecules interact only with the solvent molecules and not with one another, so that the study of the dynamics of a dilute solution of polymers reduces to the investigation of the dynamics of one macromolecule surrounded by solvent molecules. At low frequencies of motion, relaxation processes with the highest relaxation times prove to be significant, whereupon the macromolecule can be treated in terms of a universal scheme, i.e. one independent of the nature of the polymer and the solvent.

W and H Kuhn, who were the pioneers of theoretical study of the behaviour of flexible macromolecules in a flowing viscous liquid, introduced into polymer physics a very simple schematic representation of the macromolecule—the dumbbell model: two Brownian particles linked by elastic (entropic) forces (Fig. 1) [1]. On this basis, they took into account all the characteristic features of the dynamics of a flexible macromolecule in a viscous liquid, such as the intramolecular friction and the mutual hydrodynamic influence of the particles, and investigated the principal characteristic features of the behaviour of dilute solutions associated with the relaxation of flexible macromolecules: viscoelasticity and optical anisotropy. Their results are qualitative, first, because the schematic representation of a macromolecule by two particles is too approximate and, second, because the study of a very simple model such as the dumbbell leads to certain difficulties, associated with the nonlinearity of the problem, which have been overcome comparatively recently [2].

At the present time, phenomena associated with relaxation processes in macromolecules are considered on the basis of the multiparticle model of the macromolecule.

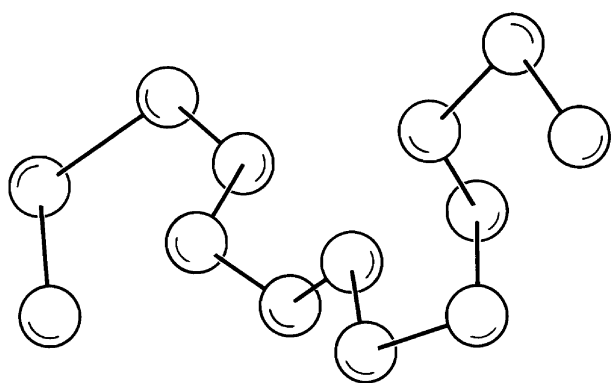
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**Figure 1.** Schematic representation of the macromolecule by a dumbbell (two Brownian particles linked by an elastic force) used in pioneer studies for the investigation of the behaviour of a flexible macromolecule in the flow of a viscous liquid.

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When slow processes are considered, the macromolecules are represented schematically, after Kargin and Slonimskii [3] and Rouse [4], by a set of linearly connected Brownian particles (Fig. 2). The study of the problem of the behaviour of such a chain in a deformable viscous liquid taking into account the bulk-phase interactions, the hydrodynamic influence of the particles on one another, and the internal friction led to a quantitative description of the effects associated with the slowest relaxation of the macromolecules, which can in fact be described solely on the basis of the universal, i.e. independent of the chemical structure, schematic representation of the macromolecule in the form of a chain of Brownian particles. For the investigation of the relaxation processes with short relaxation times, it is essential to use more detailed ideas about the macromolecule which are no longer universal but reflect the specific architecture of the macromolecule [5].



**Figure 2.** Universal schematic representation of the macromolecule by an assembly of Brownian particles linearly connected by elastic forces — the subchains model.

The theory of relaxation processes in a dilute solution is based on the theory of Brownian motion and reduces to the consideration of systems of stochastic equations and the calculation of average quantities. The formulation of the problem became completely clear in the 1950s but technical difficulties could nevertheless be overcome only when several decades had elapsed—after the application of modern methods of theoretical physics to the solution of the problem.

At low concentrations, the above simple schematic representation of the macromolecule as a collection of linearly connected Brownian particles taking into account the intramolecular friction, the volume effects, and the hydrodynamic interaction leads to a quantitative description of the observed viscoelastic and double refraction effects at comparatively low frequencies. At higher frequencies, the universal description is qualitative: there is a possibility of the appearance of effects associated with the characteristics of the detailed structure of the macromolecules.

The effects of the viscoelasticity and optical anisotropy of the dilute solution of polymers, which will be discussed further in the present review, reflect the structure and properties of an individual macromolecule and are therefore used in the study of newly synthesised polymers or polymers isolated from natural materials. Under these conditions, the more dilute the solution the easier the

interpretation of the results, since the so-called characteristic values of the measured quantities (see Section 4.2), which are independent of the concentration  $c$  (at  $c \rightarrow 0$ ), are usually considered and discussed. The theoretical results make it possible to compare these quantities with the characteristics of an individual macromolecule.

Solutions of polymers at nonzero concentrations, when the macromolecular coils interact with one another, are not of interest merely as a means of studying macromolecules but are of intrinsic interest as macromolecular systems with unusual dynamic properties which have no analogues among low-molecular-weight systems. Analysis of the dynamics of macromolecules in a system of intertwined chains naturally proved more complex but in the limit of very high concentrations ( $c \rightarrow 1$ ) the system is convenient to study: the equation for the dynamics of the macromolecule can be formulated in such a way that the generalised equation is a reliable basis for the construction of a theory of the dynamic behaviour of systems concentrated to the maximum extent.

From the standpoint of the vigorously developing theory of nonlinear dynamic phenomena [58–60], the results under discussion constitute a simple example of a system of stochastic equations defining the motion of connected Brownian particles. The study of systems of this kind demonstrated that the model reflects the characteristic features of the thermal motion of the macromolecule in both dilute and concentrated solutions (the latter case is discussed in the Conclusions) and therefore the system considered constitutes one of the most fundamental models used in the theory of the behaviour of high-molecular-weight substances.

## 2. Thermodynamics of the macromolecule

A detailed description of the microstate of the macromolecule is achieved by specifying sequences of atoms, bond lengths, bond angles, angles of the rotation of neighbouring atoms about bonds, rotation potentials, etc. The statistical theory of long chains, developed in considerable detail and described in a series of monographs [6–8], defined the equilibrium average quantities, characterising the macromolecular coil as a whole, as functions of the microparameters of the macromolecule. However, the characteristics of the macromolecule as a whole can be found on the basis of more approximate models representing the macromolecule.

### 2.1 Universal models of the macromolecule

Since the length of the macromolecule exceeds by many orders of magnitude its transverse dimensions, the macromolecule can be represented as a flexible homogeneous elastic filament with an elasticity coefficient  $a$  taking into account the individual properties of the macromolecule [7–9]. Consideration of the thermal fluctuations of the macromolecule leads to a dependence of the mean square distance between the ends of the macromolecule  $\langle R^2 \rangle_0$  on its length  $M$  and temperature  $T$ . For  $MT \gg a$ , we have

$$\langle R^2 \rangle_0 = \frac{2Ma}{T}. \quad (2.1)$$

The last relation demonstrates that at high temperatures long macromolecules are coiled up; the more coiled they are, smaller the rigidity coefficient  $a$ .

The continuous filament model considered is also called the persistent length model. The quantity  $a/T$ , where  $T$  is the temperature expressed in energy units, is called the persistent length [7, 8].

In another universal method for the description of a long macromolecule, which is applicable at high temperatures, one begins with the fact that for large distances along the macromolecule there is no correlation of the orientations of individual parts and the real chain may be compared with a chain of consecutively connected freely rotating segments, as was done for the first time by Kuhn [6].

The expression for the mean square of the distance between the ends of the macromolecule can be formulated in this case by analogy with a wandering Brownian particle as follows:

$$\langle R^2 \rangle_0 = zl^2, \quad (2.2)$$

where  $z$  is the number of chain segments and  $l$  is the length of the segment. The length of the segment may be arbitrary but must naturally be greater than atomic dimensions. To make the treatment unambiguous, an additional condition is established, which may require that

$$zl = M. \quad (2.3)$$

Eqns (2.2) and (2.3) define the freely jointed chain model [6–8].

Thus, two procedures are used for the universal description of macromolecules: the description with the aid of a flexible filament and the description with the aid of a freely jointed chain. In both cases the calculated mean square distance between the ends of the macro molecule  $\langle R^2 \rangle_0$  is small compared with the overall length of the macromolecule: regardless of its chemical structure, a sufficiently long macromolecule coils up as a consequence of thermal fluctuations so that  $\langle R^2 \rangle_0$  becomes proportional to the length of the macromolecule:

$$\langle R^2 \rangle_0 \sim M. \quad (2.4)$$

For a fixed distance  $R$  between the ends of the macromolecule, one can formulate a distribution function on this or another basis [6–8]. In the simplest case, it has the form of the Gaussian distribution.

$$W(R) = \left( \frac{3}{2\pi\langle R^2 \rangle_0} \right)^{3/2} \exp\left( -\frac{3R^2}{2\langle R^2 \rangle_0} \right). \quad (2.5)$$

## 2.2 The model of Gaussian subchains

The description of the macromolecule with the aid of one quantity—the mean square distance between its ends  $\langle R^2 \rangle_0$ —is not always sufficient. For very long macromolecules, use is made, after Kargin and Slonimskii [3] and Rouse [4], of a more detailed but also macroscopic and universal method of description in which the macromolecule is divided into  $N$  subchains each with a length  $M/N$ . The coordinates of the ends of the macromolecule and of the points corresponding to the divisions between the subchains constituting the macromolecule are numbered successively from 0 to  $N$  and are designated by  $\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^N$ .

Assuming that each subchain is also sufficiently long and may be described in the same way as the entire chain, we formulate the equilibrium distribution function for the

probabilities of the locations of all the particles constituting the macromolecule as derivatives of  $N$  distribution functions of type (2.5):

$$W(\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^N) = C \exp(-\mu A_{xy} \mathbf{r}^\alpha \mathbf{r}^\gamma), \quad (2.6)$$

where

$$\mu = \frac{3}{2b^2} = \frac{3N}{2\langle R^2 \rangle_0}, \quad (2.7)$$

while the matrix  $A_{xy}$  assumes the form

$$A_{xy} = \begin{vmatrix} 1 & -1 & 0 & \dots & 0 \\ -1 & 2 & -1 & \dots & 0 \\ 0 & -1 & 2 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 1 \end{vmatrix}. \quad (2.8)$$

The free energy of the macromolecule is then given by an expression of the following form:

$$F(\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^N) = \mu T A_{xy} \mathbf{r}^\alpha \mathbf{r}^\gamma. \quad (2.9)$$

It defines the force acting on a unit numbered  $v$  to within the first-order terms in  $\mathbf{r}$ .

$$K_i^v = -\frac{\partial F}{\partial \mathbf{r}_i^v} = -2\mu T A_{vy} \mathbf{r}_i^y. \quad (2.10)$$

There is a possibility of various extensions of the Gaussian subchain model: if it is necessary to take into account the additional rigidity of the chain in relation to bending, one has to add the interaction between the individual units and the matrix (2.8) is replaced, for example, by a pentadiagonal matrix. It is also possible to take into account the finite extendability of the subchains. For this purpose, higher-order terms in  $\mathbf{r}$  are added to Eqn (2.9), etc.

The Gaussian subchain model defined in this way and its possible extensions are universal and are applicable to all sufficiently long flexible macromolecules regardless of their chemical nature. By virtue of its universality, the model considered plays a fundamental role in the theory of the equilibrium and nonequilibrium properties of polymers. For  $N = 1$ , the subchains model is converted into the simplest model of a flexible macromolecule—a dumbbell comprising two spheres linked by an elastic force. As already mentioned, this model was introduced and used by Kuhn and Kuhn [1] to elucidate the characteristic features of the dynamics of the macromolecule in a flow.

We may note in conclusion that, for high values of  $N$ , one may use the variable

$$s = \frac{\alpha}{N+1}, \quad 0 \leq s \leq 1,$$

and the matrix introduced in this Section written in the form

$$A_{xy} \approx -\frac{1}{N^2} \frac{d^2}{ds^2},$$

which makes it possible to represent the formulae discussed here in another way.

## 2.3 Normal coordinates

In terms of the Gaussian subchains approximation, the distribution function (2.6) makes it possible to calculate all

the equilibrium characteristics of the macromolecular coil, for example the average value of the square of the radius of inertia of the coil:

$$\langle S^2 \rangle = \frac{1}{1+N} \sum_{\alpha=0}^N \langle |r^\alpha - q|^2 \rangle, \quad q = \frac{1}{1+N} \sum_{\alpha=0}^N r^\alpha. \quad (2.11)$$

However, for calculations in this and many other cases it is convenient to employ new variables, referred to henceforth in accordance with tradition as the normal coordinates and introduced by means of the relations

$$r^\beta = Q_{\beta\alpha} \rho^\alpha, \quad \rho^\alpha = Q_{\alpha\gamma}^{-1} r^\gamma, \quad (2.12)$$

as well as variables such that the quadratic form in Eqns (2.6) and (2.9) assumes the diagonal form, so that

$$Q_{\lambda\mu} A_{\lambda\gamma} Q_{\gamma\beta} = \lambda_\mu \delta_{\mu\beta}. \quad (2.13)$$

It is readily seen that the determinant of the matrix  $A$  is zero, so that one of the eigenvalues, say  $\lambda_0$ , is always zero. The normal coordinate corresponding to the zero eigenvalues

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

is proportional to the coordinate of the centre of gravity of the macromolecular coil  $q$  defined by Eqn (2.11).

In considering the behaviour of the macromolecule, it is convenient to use a coordinate system with the origin at the centre of gravity of the system. Then  $\rho^0 = 0$ , so that in this instance there are only  $N$  normal coordinates numbered from 1 to  $N$ .

The distribution function (2.6), normalised to unity, now assumes the following form in terms of normal coordinates:

$$W(\rho^1, \rho^2, \dots, \rho^N) = \prod_{\gamma=1}^N \left( \frac{\mu \lambda_\gamma}{\pi} \right)^{3/2} \exp(-\mu \lambda_\gamma \rho^\gamma \rho^\gamma). \quad (2.14)$$

With the aid of this distribution function, it is easy to calculate the equilibrium moments of the normal coordinates:

$$\langle \rho_i^\nu \rho_k^\nu \rangle = \int W \rho_i^\nu \rho_k^\nu \{d\rho\} = \frac{1}{2\mu \lambda_\nu} \delta_{ik},$$

through which one can express, for example, the mean square radius of inertia defined by Eqn (2.11):

$$\langle S^2 \rangle_0 = \frac{1}{1+N} \sum_{\alpha=1}^N \langle \rho_i^\alpha \rho_k^\alpha \rangle \approx \frac{1}{6} \langle R^2 \rangle_0.$$

The calculation of higher-order moments, for example fourth-order moments, does not present special difficulties either:

$$\langle \rho_i^\nu \rho_k^\nu \rho_s^\nu \rho_j^\nu \rangle_0 = \frac{1}{4(\mu \lambda_\nu)^2} (\delta_{ik} \delta_{sj} + \delta_{is} \delta_{kj} + \delta_{ij} \delta_{ks}).$$

We may note that the transformation matrix  $Q$  may be selected in different ways, in particular an orthogonal and normalised matrix may be chosen. In this case, the eigenvalues (see, for example, Dean [10]) assume the following form for high values of  $N$  and small numbers  $\alpha$ :

$$\lambda_\alpha = \left( \frac{\pi \alpha}{N} \right)^2, \quad \alpha = 0, 1, 2, \dots \ll N. \quad (2.15)$$

In the case of the orthogonal transformation, the relation between the normal coordinate  $\rho^0$ , corresponding to the zero eigenvalue, and the coordinate of the centre of gravity of the macromolecule is formulated thus:

$$\rho^0 = q(1+N)^{1/2}. \quad (2.16)$$

## 2.4 The excluded volume effects

The above results are valid for a free noninteracting noncorporeal chain, which is an extremely useful idealisation. However, the atoms of the macromolecule interact with one another and the primary result of this interaction is that parts of the macromolecule cannot occupy the volume occupied by any other parts, i.e. the probabilities of consecutive steps are no longer statistically independent as is assumed in the derivation of the above distribution functions for the probability and for the mean square distance between the ends of the macromolecule [11, 12]. For the subchains model, considered in the previous Section, the distribution function at equilibrium and when account is taken of the potential of the interaction between the particles can be expressed in the form

$$W = C \exp\left(-\mu A_{\alpha\gamma} r^\alpha r^\gamma - \frac{1}{T} U\right), \quad (2.17)$$

where  $C$  is the normalisation constant and  $U$  the energy of the 'lateral' interactions, which depends on the difference between the coordinates of the particles and may be represented fairly accurately by pair interactions:

$$U = \sum_{\gamma \neq \nu} U(|r^\gamma - r^\nu|).$$

The constant  $\mu$  may be expressed in terms of the mean square distance between the ends of the subchain when account is taken of the  $b^2$  interactions. From considerations of dimensionality, we then have

$$\mu \sim b^{-2}.$$

The average value of the square of the distance between the ends of the entire chain  $\langle R^2 \rangle$  is determined by the 'lateral' interaction, which is characterised by the second virial coefficient  $B(T)$  (also temperature-dependent) and can now be expressed in the following form taking into account the considerations of dimensionality:

$$\langle R^2 \rangle = N b^2 f(N, B(T) b^{-3}).$$

Naturally, the form of the dependence of the quantity  $\langle R^2 \rangle$  on the arbitrary number of subdivisions  $N$  ( $N \rightarrow \infty$ ), which is not related to any other characteristics of the macromolecules, is independent of  $N$  and one must therefore assume that  $B(T)/b^3$  does not change when the number of subdivisions is altered, while the function of the number of subdivisions must be formulated as a power function:

$$\langle R^2 \rangle = N^{2\nu} b^2. \quad (2.18)$$

Thus, fairly general considerations lead to the establishment of a power dependence of the mean square size of the macromolecule on its length:

$$\langle R^2 \rangle \sim M^{2\nu}, \quad \nu \geq 1/2. \quad (2.19)$$

Taking into account the relations formulated above, the expression for the elasticity coefficient of the subchain when

account is taken of the volume effects can be written as follows:

$$\mu \sim \left(\frac{N}{M}\right)^{2\nu}. \quad (2.20)$$

The determination of the power exponent  $2\nu$  in the above expressions requires special and not very simple calculations [12]. From the simplest hypotheses, it has been found that [12, 13].

$$2\nu = \frac{9}{8}.$$

Thus, when account is taken of volume effects, the size of the macromolecular coil exceeds the size of the ideal coil.

We may note that the second virial coefficient generally speaking does not depend on temperature. At high temperatures, repulsion predominates between the monomers, while at low temperatures attraction predominates, so that there is a temperature, referred to as the  $\Theta$ -temperature, at which the attraction and repulsion effects cancel out and  $B(T) = 0$ . It is usually assumed [11] that at this point the macromolecule is described by the relations for an ideal chain, which were indicated in the previous Sections.

### 2.5 The macromolecule in a solvent

Next we shall consider solutions of polymers which are so dilute that the macromolecules can be regarded as not interacting with one another. In such a solution, the macromolecules do not form aggregates and therefore one should consider in the first place the behaviour of a single macromolecule surrounded by solvent molecules. Apart from the interaction between the parts of a single macromolecule, it is now necessary to take into account such interactions between the macromolecule and the solvent.

In the subchains approximation, the equilibrium distribution function of the particle coordinates again assumes the form (2.17) under these conditions, but the potential  $U$  of the energy of the 'lateral' interaction of the particles is now an effective potential which takes into account the interaction of the atoms of the macromolecule with one another and with the solvent atoms.

In solvents referred to as good, the polymer-solvent contacts are energetically more favourable than the polymer-polymer and solvent-solvent contacts, so that the molecular coil tends to swell. In poor solvents, the opposite situation occurs and the macromolecular coil tends to contract [14, 15].

The second virial coefficient of the macromolecule  $B(T)$  now depends not only on the temperature but also on the type of solvent. If a solvent such that  $B(T) = 0$  has been found at a specified temperature  $T$ , it is referred to as a  $\Theta$ -solvent. In such a solvent, the size of the macromolecular coil is the same as the size of the ideal coil, i.e. one where no account is taken of volume effects.

## 3. Dynamics of the macromolecule in a viscous liquid

On the basis of the subchains model, we shall consider in this section the dynamics of the macromolecule, and the relaxation equations for the macromolecule moving in a viscous liquid with a viscosity  $\eta^0$  for specified constant velocity gradients will be derived:

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

It will be convenient to employ henceforth the following notation for symmetrised and antisymmetrised velocity gradients:

$$\gamma_{ij} = \frac{1}{2}(v_{ij} + v_{ji}), \quad \omega_{ij} = \frac{1}{2}(v_{ij} - v_{ji}).$$

The characteristics of long macromolecules as macro-systems make it possible to employ a phenomenological procedure for the description of relaxation processes, which permits the formulation of overall results regardless of the extent to which the mechanism of a particular effect is understood.

### 3.1 Hydrodynamic interaction of the particles of the macromolecular coil

In the study of the dynamics of the macromolecule in the subchains approximation, each subchain with a length  $M/N$  ( $N$  is the number of subchains) is likened to a Brownian particle and each particle, moving at a velocity  $u^j$ , is acted upon by the hydrodynamic entrainment force, which according to Stokes has the form

$$F_j^\gamma = -\zeta_0(u_j^\gamma - v_j^\gamma), \quad (3.1)$$

where  $\zeta_0 = 6\pi\eta^0 a$  is the coefficient of resistance and  $v_j^\gamma$  the velocity of the liquid in which the given particle is present, the velocity corresponding to the situation where no account is taken of the particle. When an assembly of particles is considered, the velocity  $v_j^\gamma$  is generally speaking determined by the motion of all the particles considered. For the slowest motions, we have in the Stokes approximation [16]

$$v_j^\gamma = v_{jl}r_l^\gamma - \sum_{\beta=0}^N T_{jl}^{\gamma\beta} F_l^\beta.$$

The components of the hydrodynamic interaction tensor  $T_{jl}^{\gamma\beta}$  for  $\gamma = \beta$  are zero, while in the case where  $\gamma \neq \beta$  they are determined by the relation

$$T_{ik}^{\gamma\beta} = \frac{1}{8\pi\eta^0 |\mathbf{r}^\gamma - \mathbf{r}^\beta|} (\delta_{ik} + e_i^{\gamma\beta} e_k^{\gamma\beta}), \quad (3.2)$$

where  $e_i^{\gamma\beta} = (r_i^\gamma - r_i^\beta)/|\mathbf{r}^\gamma - \mathbf{r}^\beta|$ .

A system of equations for the entrainment forces follows from Eqns (3.1) and (3.2):

$$F_j^\alpha = -\zeta_0(u_j^\alpha - v_{jl}r_l^\alpha) - \zeta_0 \sum_{\beta} T_{jl}^{\alpha\beta} F_l^\beta. \quad (3.3)$$

For small perturbations, the solution of Eqns (3.3) assumes the following form to a first approximation:

$$F_j^\alpha = -\zeta_0 \sum_{\gamma \neq \alpha} \left[ \left( \delta_{\alpha\gamma} - \frac{\zeta_0}{8\pi\eta^0} \frac{1}{|\mathbf{r}^\alpha - \mathbf{r}^\gamma|} \right) \delta_{jl} - \frac{\zeta_0}{8\pi\eta^0} \frac{e_j^{\alpha\gamma} e_l^{\alpha\gamma}}{|\mathbf{r}^\alpha - \mathbf{r}^\gamma|} \right] (u_l^\gamma - v_{li}r_i^\gamma). \quad (3.4)$$

Eqn (3.4) shows that the resistance (entrainment) force for a certain particle depends on the relative velocities of all the particles of the macromolecule and also on the relative distance between the particles.

We may note that values of the hydrodynamic interaction tensor (3.2) averaged beforehand with the aid of some kind of distribution function are frequently used for the estimation of the influence of the hydrodynamic

interaction, as has been suggested by Kirkwood and Riseman [16].

For example, after averaging with respect to the equilibrium distribution function for the ideal coil, the hydro-dynamic interaction tensor (3.2) assumes the following form [16].

$$\langle \zeta_0 T_{ij}^{\alpha\gamma} \rangle = 2h|\alpha - \gamma|^{-1/2} \delta_{ij}. \quad (3.5)$$

The dimensionless hydrodynamic direction parameter appears here:

$$h = \frac{\zeta_0 \sqrt{6/\pi}}{12\pi\eta^0 b} \approx \frac{a}{b},$$

where  $a$  is the radius of the particle associated with a subchain having a length  $M/N$  and  $b$  is the mean square distance between neighbouring particles along the chain.

### 3.2 The effective coefficient of friction

The expression for the entrainment (resistance) force [Eqn (3.4)] is valid for small mutual influences of the particles, i.e. when the hydrodynamic interaction parameter is small ( $h \ll 1$ ). In the cases of interest to us, the parameter  $h$  is not small and other methods are used for the calculation of the entrainment (resistance) force [17–19]. However, one may also demonstrate the validity of the result by a simpler procedure, which is convenient in the case where one considers, following Kirkwood's ideas [16], a hydrodynamic interaction subjected to preliminary averaging.

One may note that the forces presented, the effect of which on the particle is linear as a function of the velocity [see, for example, Eqns (3.1) and (3.4)], are associated with the low velocities of the particles and of the flow and not with the weakness of the hydrodynamic interaction, so that the expression for the force acting on a particle in the flow can be expressed in the following general form:

$$F_j^\alpha = -\zeta_0 B_{ji}^{\alpha\gamma} (u_i^\gamma - v_{il} r_l^\gamma), \quad (3.6)$$

where in the case of the preliminary averaging the hydrodynamic interaction matrix  $B_{ji}^{\alpha\gamma}$  assumes the following form according to Eqns (3.4)–(3.5) under the conditions of weak interaction:

$$B_{ji}^{\alpha\gamma} = (\delta_{\alpha\gamma} - 2h|\alpha - \gamma|^{-1/2}) \delta_{ij},$$

while for arbitrary interactions it can be represented by the equation

$$B_{jl}^{\alpha\gamma} = B_{\alpha\gamma} \delta_{jl} + V_{\alpha\gamma\beta\lambda} (\langle r_j^\beta r_l^\lambda \rangle - \langle r_j^\beta r_l^\lambda \rangle_0). \quad (3.7)$$

after introducing the new numerical matrices  $B_{\alpha\gamma}$  and  $V_{\alpha\gamma\beta\lambda}$ .

We shall not discuss here the second term, which contributes to the components in the subsequent results, which are nonlinear in the velocity gradients, and precludes the introduction of relaxation modes independent of one another.

When normal coordinates are employed, defined by Eqns (2.12), it is now possible to make use of the arbitrariness in the definition of the matrix  $Q$  and to define it in such a way that the matrix  $B_{\alpha\gamma}$  assumes a diagonal form after transformation. The problem of the simultaneous adjustment of the symmetrical matrices  $A$  and  $B$  to a diagonal form does have a solution [20]: since the matrix  $A$  is defined non-negatively and  $B$  is defined positively, it is possible to find a transformation such that  $B$  is transformed into a unit matrix and  $A$  into a

diagonal matrix. Therefore, simultaneously with Eqn (2.13), in which the eigenvalues  $\lambda_\mu$  are now defined by Eqns (2.15) and the expression which we shall discuss below, one can write

$$\zeta_0 Q_{\alpha\lambda} B_{\alpha\gamma} Q_{\gamma\nu} = \zeta \delta_{\lambda\nu}. \quad (3.8)$$

This relation introduces the effective coefficient of friction of the particles  $\zeta$ , the dependence of which on the length of the macromolecule is of special interest.

In the case where the hydrodynamic interaction of the particles of the macromolecule may be neglected, i.e. when the coil is, as it were, permeable, the coefficient of resistance of the latter is proportional to the length of the macromolecule and the coefficient of friction of the particle associated with the length  $M/N$  is proportional to this length:

$$\zeta \sim \frac{M}{N}. \quad (3.9)$$

The mutual influence of the particles leads to their shielding within the coil and the overall coefficient of the resistance of the coil proves to be smaller than for a permeable coil.

The requirement of covariance in relation to successive subdivisions of the macromolecule into subchains gives rise to the following power dependence for high values of  $N$ :

$$\zeta \sim \left( \frac{M}{N} \right)^{(z-2)\nu}. \quad (3.10)$$

In order to calculate the power exponents, a calculation based on specific representations is necessary, as in the case where account is taken of volume effects. The exponents calculated by Al-Noami et al. [17] are listed in Table 1. We may note that these results are valid for infinitely long chains, so that the exponents for finite chains may also assume intermediate values.

**Table 1.** The exponents in the asymptotic formulae.

Allowance for volume effects	Allowance for impermeability	$2\nu$	$z$	$(z-2)\nu$	$z\nu$
+	–	9/8	15.4	63/64	2.11
–	+	1	3	1/2	1.5
+	+	9/8	3	9/16	1.69
–	–	1	4	1	2

### 3.3 Intramolecular friction

On deformation of the macromolecule, i.e. when the particles constituting the chain are involved in relative motion, an additional dissipation of energy takes place and intramolecular friction forces appear. In the simplest case of a chain with two particles (a dumbbell), the force associated with the internal viscosity is proportional to the relative velocity of the ends of the dumbbell  $u_j'' - u_j'$  and is given by [1, 15, 21]

$$-\kappa(u_j'' - u_j') e_j e_i, \quad (3.11)$$

where  $e$  is a unit vector in the direction of the vector connecting the particles of the dumbbell and  $\kappa$  is the phenomenological internal friction coefficient.

When a multisegmental model of the macromolecule (the Slonimskii–Kargin–Rouse model) is considered, one must assume that the force acting on each particle is determined by the difference between the velocities of all the particles  $u_j^\alpha - u_j^\beta$ . These quantities must be introduced in such a way that dissipative forces do not arise on rotation of the macromolecular coil as a whole, whereupon  $u_j^\alpha = \Omega_{jl} r_l^\alpha$ , thus the internal friction force must be formulated as follows in terms of a general linear approximation:

$$G_i^\alpha = - \sum_{\beta \neq \alpha} C^{\alpha\beta} (u_j^\alpha - u_j^\beta) e_j^{\alpha\beta} e_i^{\alpha\beta},$$

where  $e_j^{\alpha\beta} = (r_j^\alpha - r_j^\beta) / |r^\alpha - r^\beta|$ . The matrix  $C^{\alpha\beta}$  is symmetrical and may depend on the distance between the particles, but we shall assume henceforth that a preliminary averaging has been carried out so that  $C^{\alpha\beta}$  is a numerical matrix. The diagonal terms of the matrix are zero.

The internal friction force can also be written in the form

$$G_i^\alpha = -G_{ij}^{\alpha\gamma} u_j^\gamma, \quad (3.12)$$

where the matrix

$$G_{ij}^{\alpha\beta} = \delta_{\alpha\beta} \sum_{\gamma \neq \alpha} C^{\alpha\gamma} e_i^{\alpha\gamma} e_j^{\alpha\gamma} - C^{\alpha\beta} e_i^{\alpha\beta} e_j^{\alpha\beta} \quad (3.13)$$

has been introduced. In contrast to the matrix  $C^{\alpha\beta}$ , the matrix  $G^{\alpha\beta}$  has nonzero diagonal terms.

Eqn (3.12) defines the intramolecular friction force, but the requirement that the force remains unchanged on rotation of the macromolecular coil as a whole is fulfilled only for a particular choice of the friction matrix  $G_{ij}^{\alpha\beta}$ . When an attempt is made to simplify Eqn (3.13) by preliminary averaging, we obtain the following expression for the force instead of Eqn (3.12):

$$G_i^\alpha = -G^{\alpha\gamma} u_i^\gamma,$$

which clearly does not satisfy the above requirement.

On linearisation of the internal friction force according to Cerf's procedure [22], Eqn (3.12) may be modified and written thus:

$$G_i^\alpha = -G^{\alpha\gamma} (u_j^\gamma - \Omega_{jl} r_l^\gamma), \quad (3.14)$$

where  $G^{\alpha\gamma}$  is now a symmetrical numerical matrix.

The rate of rotation of the macromolecular coil in a flow  $\Omega_{jl}$  is determined by the velocity gradients:

$$\Omega_{jl} = \omega_{jl} + A_{jlsk} \gamma_{sk}.$$

When linear effects are considered, the matrix  $A_{jlsk}$  can be determined by considering the average rotation of the coil subjected to equilibrium averaging. Since at equilibrium the coil is spherical, it follows from symmetry conditions that

$$\Omega_{jl} = \omega_{jl}$$

to within first-order terms.

In terms of the normal coordinates introduced by Eqn (2.12), the matrix associated with the internal friction can be written as follows:

$$Q_{\alpha\lambda} G_{ij}^{\alpha\gamma} Q_{\gamma\mu}.$$

By considering the transformed expression for the internal friction force (3.12) as a nonlinear function of the normal coordinates and a unit vector referring to a separate normal coordinate

$$e_i^\lambda = \rho_i^\lambda |\rho^\lambda|^{-1},$$

one may note that the requirement that the internal viscosity force disappears when the whole coil is rotated is satisfied by a unique combination of variables, so that the term with the internal viscosity expressed in normal coordinates becomes

$$-\zeta \gamma_\alpha e_i^\alpha e_j^\alpha \dot{\rho}_j^\alpha. \quad (3.15)$$

For the linearised version (3.14), we have

$$-\zeta \gamma_\alpha (\dot{\rho}_j^\alpha - \omega_{jl} \rho_l^\alpha), \quad (3.16)$$

where  $\zeta$  is the effective coefficient of friction.

It is noteworthy that the representation of the force in the form of Eqn (3.16) is possible only for weak intramolecular friction ( $\gamma_\alpha \ll 1$ ), whereas Eqn (3.15) is also valid for arbitrarily large intramolecular friction. For low values of  $\gamma_\alpha$ , the results of the calculations are independent of which expression, (3.15) or (3.16), is used.

The characteristic  $\gamma_v$  of the intramolecular friction forces in Eqns (3.15) and (3.16), introduced here as a phenomenological quantity, should not depend on the method of subdivision of the macromolecule into subchains and, by virtue of the nature of the transformation, should be a function of the ratio  $v/M$ . Here one may expect that  $\gamma_v$  is a monotonically increasing function of the number of the mode  $v$ . This dependence can be fitted by the power function

$$\gamma_v = \gamma_1 v^\Theta \sim \left(\frac{v}{M}\right)^\Theta, \quad \gamma_1 \sim M^{-\Theta}, \quad (3.17)$$

where  $\Theta$  is a positive number and  $\gamma_1$  is a measure of the internal viscosity.

The internal viscosity force is defined phenomenologically by Eqns (3.15) and (3.16) formulated above. Various internal-friction mechanisms, discussed in a number of studies [23–26], are possible. Their consideration leads to the determination of the matrices  $C^{\alpha\beta}$  and  $G^{\alpha\beta}$  and to the nature of the dependence of the internal friction coefficients on the chain length and the parameters of the macromolecule.

The significance and importance of the internal friction coefficient  $\gamma_\alpha$  introduced in this way can be elucidated by comparing the consequences of the theory with experimental data, which will be discussed below. However, here one should note that the phenomenological characteristics of the intramolecular friction prove to depend not only on the characteristics of the macromolecule, as might have been expected, but also on the properties of the liquid in which the macromolecule is present.

The internal viscosity of the macromolecule is a consequence of the intramolecular relaxation processes occurring on deformation of the macromolecule at a finite rate. The very introduction of the internal viscosity is possible only insofar as the deformation times are short compared with the relaxation times of the intramolecular processes. At deformation frequencies of the same order of magnitude as the reciprocal of the relaxation time, these relaxation processes must be taken into account in considering the dynamics of the macromolecule and the dynamics of a dilute solution of polymers [27].

### 3.4 Equation of motion of the macromolecule

After considering the dissipative forces acting on the particles of the chain, we shall now formulate and discuss the equation for the dynamics of the macromolecule in the flow of a viscous liquid with constant velocity gradients  $v_{ij} = \partial v_i / \partial x_j$  [28].

Apart from dissipative forces, elastic forces acting on the particle are taken into account in formulating the dynamic equation:

$$\mathbf{K}^\alpha = -\frac{\partial F}{\partial \mathbf{r}^\alpha} = -2T\mu A_{xy} \mathbf{r}^\gamma - \frac{\partial U}{\partial \mathbf{r}^\alpha} \quad (3.18)$$

as well as random forces  $\Phi_i^\alpha$ , associated with thermal motion, which leads to the formulation

$$m \frac{d^2 \mathbf{r}^\alpha}{dt^2} = \mathbf{F}^\alpha + \mathbf{G}^\alpha + \mathbf{K}^\alpha + \Phi_i^\alpha, \quad \alpha = \overline{0, N}, \quad (3.19)$$

where the expressions for the dissipative forces  $\mathbf{F}^\alpha$  and  $\mathbf{G}^\alpha$  are defined by Eqns (3.6) and (3.12) formulated previously.

In terms of the normal coordinates introduced previously and taking into account all the considerations described above, the dynamic equation becomes

$$Q_{\gamma\alpha} Q_{\gamma\mu} m \frac{d^2 \rho_i^\mu}{dt^2} = -\zeta(\dot{\rho}_i^\alpha - v_{ij} \rho_j^\alpha) - \zeta \gamma_\alpha e_i^\alpha e_j^\alpha \dot{\rho}_j^\alpha - 2\mu T \lambda_\alpha \rho_i^\alpha + \xi_i^\alpha, \quad \alpha = 1, 2, \dots, N, \quad (3.20)$$

where  $\xi_i^\alpha = Q_{\gamma\alpha} \Phi_i^\gamma$ .

The transformations matrix  $Q_{\alpha\gamma}$  is not generally speaking orthogonal and the left-hand side of the equation formulated therefore includes the derivatives of all the coordinates, but we shall not dwell on this factor bearing in mind that in the limit  $m \rightarrow 0$  which we are interested in the left-hand side of the equation vanishes.

At the above limit, Eqn (3.20) defines independent relaxation modes of the macromolecule. The equation of motion for each mode represents the equation of motion of a dumbbell with intrinsic elasticity and internal friction coefficients.

The behaviour of modes with small numbers should be independent of the arbitrary number of subdivisions  $N$ . This means that the relation

$$\frac{\zeta}{\mu \lambda_\alpha}$$

should not depend on  $N$ . Since the dependence of the quantities  $\mu$  and  $\zeta$  on the number of subdivisions was elucidated previously [Eqns (2.20) and (3.10)], the above requirement immediately leads to the expression

$$\lambda_\alpha \sim \left(\frac{\alpha}{N}\right)^{zv}, \quad \alpha = 1, 2, \dots, \ll N. \quad (3.21)$$

The values of  $z$  and  $v$  for four cases are presented in Table 1. For a permeable molecule, where  $zv = 2$ , the eigenvalues (3.21) are defined by Eqn (2.15).

The random force  $\Phi_i^\gamma$  in the dynamic Eqns (3.19) and (3.20) is determined as an average quantity and is selected from the condition that the equilibrium coordinates and velocities are known beforehand [29]. In the linearised version with  $\gamma_\alpha \ll 1$ , this requirement determines the relation

$$\langle \xi_i^\alpha(t) \xi_j^\gamma(t') \rangle = 2T\zeta(1 + \gamma_\alpha) \delta_{xy} \delta_{ij} \delta(t - t'). \quad (3.22)$$

which is valid to within first-order terms in velocity gradients. Here and henceforth the angular brackets indicate averaging with respect to the assembly of realisations of the random force.

### 3.5 The distribution function

Eqn (3.20) for the dynamics of the macromolecule is a nonlinear stochastic equation for normal coordinates and rates of change of the latter:  $\rho_i^v$  and  $\dot{\rho}_i^v$  ( $i = \overline{1, 3}, v = 1, 2, \dots, N$ ). An estimate shows that for the particles of the subchains model under consideration, the inertial effects are insignificant and one can therefore confine the treatment to the consideration of the probability of the distribution of coordinates:

$$W(t, \mathbf{r}^0, \dots, \mathbf{r}^N) = \langle \delta(\mathbf{r}^0 - \mathbf{r}^0(t)) \dots \delta(\mathbf{r}^N - \mathbf{r}^N(t)) \rangle. \quad (3.23)$$

The distribution function satisfies [29] the continuity equation

$$\frac{\partial W}{\partial t} + \sum_{\alpha=1}^N \frac{\partial \psi_j^\alpha W}{\partial \rho_j^\alpha} = 0, \quad (3.24)$$

where  $\psi_j^\alpha = \langle \dot{\rho}_j^\alpha \rangle$  is the rate of diffusion of the particle in the coordinate space, which is determined by means of the equation for the dynamics of the particles involving the introduction of an average thermal 'force'— $T \partial \ln W / \partial \rho_j^\alpha$  instead of the random force.

Calculations [21, 28, 30] have led to the derivation of the diffusion equation for the distribution function:

$$\begin{aligned} \frac{\partial W}{\partial t} + \sum_{v=1}^N \left[ -\frac{T}{\zeta} \frac{\partial^2 W}{(\partial \rho_i^v)^2} + \frac{T}{\zeta} \frac{\gamma_v}{1 + \gamma_v} \left( \frac{2\rho_i^v}{\rho_j^v \rho_j^v} \frac{\partial W}{\partial \rho_i^v} + e_s^v e_j^v \frac{\partial^2 W}{\rho_j^v \partial \rho_j^v} \right) - \frac{2\mu T}{\zeta} \frac{\lambda_v}{1 + \gamma_v} \left( 3W + \rho_j^v \frac{\partial W}{\partial \rho_j^v} \right) + v_{js} \rho_s^v \frac{\partial W}{\partial \rho_j^v} - \frac{\gamma_v}{1 + \gamma_v} e_s^v e_i^v v_{si} \left( 3W + \rho_j^v \frac{\partial W}{\partial \rho_j^v} \right) \right] = 0. \end{aligned} \quad (3.25)$$

When there are no velocity gradients, the solution of Eqn (3.25) normalised with respect to unity has the form of Eqn (2.14). In the general case for low velocity gradients, the time independent distribution function may be found in the form of an expansion in terms of invariant combinations of the vector  $\mathbf{r}^v$  and the symmetrised and antisymmetrised velocity gradient tensors  $\gamma_{ik}$  and  $\omega_{ik}$ . In the stationary case, we have, to within the second-order terms in the velocity gradients

$$W = W_0 \left\{ 1 + \sum_{v=1}^N \left[ 2\mu \lambda_v \tau_v \gamma_{ik} \rho_i^v \rho_k^v + 2(\mu \lambda_v \tau_v)^2 \gamma_{ik} \gamma_{sj} \rho_i^v \rho_k^v \rho_s^v \rho_j^v - \tau_v^2 \gamma_{ik} \gamma_{ik} - 16G_v (\mu \lambda_v \tau_v)^2 \gamma_{si} \omega_{sk} \rho_i^v \rho_k^v \right] \right\}, \quad (3.26)$$

where  $W_0$  is defined by Eqn (2.14) and the following notation for the relaxation time has been introduced:

$$\tau_\alpha = \frac{\zeta}{4T\mu\lambda_\alpha} = \tau_1 \alpha^{-zv}, \quad (3.27)$$



where  $\tau_1 = \zeta/4T\mu\lambda_1$  is the characteristic relaxation time equal to the maximum relaxation time of the macromolecule. By virtue of Eqns (2.20), (3.10), and (3.21), the characteristic relaxation time is independent of the number of subdivisions and depends on the length of the macromolecule  $M$  as follows:

$$\tau_1 \sim M^{2\nu} . \tag{3.28}$$

In Eqn (3.26), the coefficient of the last term  $G_\nu$  depends on the scalar  $\rho_j^y \rho_j^y$  and the internal viscosity. If  $\gamma_\nu = 0$ , then

$$G_\alpha = \frac{1}{4\mu\lambda_\alpha} . \tag{3.29}$$

For higher values of the internal viscosity, where  $\gamma_\nu \gg 1$ , we have

$$G_\nu = \frac{1}{6} \rho_j^y \rho_j^y + \frac{1}{9\gamma_\nu} \rho_j^y \rho_j^y (5 - 2\lambda_\nu \mu \rho_j^y \rho_j^y) + \frac{1}{27\gamma_\nu^2} \rho_j^y \rho_j^y [35 - 56\lambda_\nu \mu \rho_j^y \rho_j^y + 12(\lambda_\nu \mu \rho_j^y \rho_j^y)^2] . \tag{3.30}$$

### 3.6 Relaxation equations

The distribution function (3.26) considered in the previous Section makes it possible to calculate the moments in the stationary case, for example the second-order moments

$$\langle e_i^y e_k^y \rangle = \int W e_i^y e_k^y \{d\rho\} , \quad \langle \rho_i^y \rho_k^y \rangle = \int W \rho_i^y \rho_k^y \{d\rho\} .$$

In the general case, it is more convenient to determine the moments from equations which can be derived directly from the diffusion equation (3.25) [21, 28, 30].

For example, on multiplying Eqn (3.25) by  $\rho_i \rho_k$  (to simplify the formulation, the mode index has been omitted) and integrating with respect to all the variables, we find the relaxation equation

$$\begin{aligned} \frac{d\langle \rho_i \rho_k \rangle}{dt} = & -\frac{1}{\tau} \frac{3}{2\mu\lambda} \left( \langle e_i e_k \rangle - \frac{1}{3} \delta_{ik} \right) \\ & - \frac{1}{\tau'} \left( \langle \rho_i \rho_k \rangle - \frac{3}{2\mu\lambda} \langle e_i e_k \rangle \right) + v_{ij} \langle \rho_j \rho_k \rangle \\ & + v_{kj} \langle \rho_j \rho_i \rangle - \frac{2\gamma}{1+\gamma} \langle \rho_i \rho_k e_j e_s \rangle v_{js} . \end{aligned} \tag{3.31}$$

Two relaxation times appear here: the first time  $\tau_\alpha$ , defined by Eqn (3.27), refers to orientation processes; the second time  $\tau'_\alpha = (1 + \gamma_\alpha)\tau_\alpha$  refers to deformation processes.

Indeed, by multiplying Eqn (3.25) by  $\rho^2$  and integrating with respect to all the variables or by carrying out a direct summation of Eqn (3.31) with identical indices, we find

$$\frac{d\langle \rho^2 \rangle}{dt} = -\frac{1}{\tau'} \left( \langle \rho^2 \rangle - \frac{3}{2\mu\lambda} \right) + \frac{2}{1+\gamma} \langle \rho_s \rho_j \rangle \gamma_{sj} . \tag{3.32}$$

This equation describes only the deformation of the macromolecular coil and therefore  $\tau'$  is the relaxation time of the deformation process. In order to isolate the orientation process, we now formulate the moments in the form

$$\langle \rho_i \rho_k \rangle = \langle \rho^2 \rangle \langle e_i e_k \rangle , \quad \langle \rho_i \rho_k e_j e_s \rangle = \langle \rho^2 \rangle \langle e_i e_k e_j e_s \rangle .$$

Then, when account is taken of the equation formulated to within first-order terms in the velocity gradients, Eqn

(3.31) gives rise to the relaxation equation for the orientation process:

$$\begin{aligned} \frac{d\langle e_i e_k \rangle}{dt} = & -\frac{1}{\tau} \left( \langle e_i e_k \rangle - \frac{1}{3} \delta_{ik} \right) + v_{ij} \langle e_j e_k \rangle \\ & + v_{kj} \langle e_j e_i \rangle - \frac{2\gamma}{1+\gamma} \langle e_i e_k e_j e_s \rangle \gamma_{js} . \end{aligned} \tag{3.33}$$

Thus  $\tau_\nu$  is the relaxation time for the orientation process and  $\tau'_\nu$  is the relaxation time for the deformation process associated with the  $\nu$ th mode of motion. Taking into account the nature of the motion on excitation of the  $\nu$ th mode, one may say also that  $\tau_\nu$  is the transverse relaxation time, while  $\tau'_\nu$  is the longitudinal relaxation time. This claim becomes significant for large numbers  $\nu$ .

We may note that, for a nonzero internal viscosity, the system of equations for the moments is found to be open: fourth-order moments are introduced into the equations for the second-order moment, etc. This situation is encountered in the theory of the relaxation of a suspension of hard particles [30]. Incidentally, for  $\gamma \rightarrow \infty$ , Eqn (3.33) becomes identical with the relaxation equation for the orientation of infinitely extended ellipsoids of rotation (Pokrovskii [30, p. 58]).

In contrast to the situation described, the system for the moments (3.31) is closed in the case where the internal viscosity may be neglected. This factor makes it possible to find the moments in the form of a series expansion for low values of the velocity gradients.

In the stationary case, the expansion assumes the form

$$\begin{aligned} \langle \rho_i^\alpha \rho_k^\alpha \rangle = & \frac{1}{2\mu\lambda_\alpha} \{ \delta_{ik} + 2\tau_\alpha \gamma_{ik} \\ & + 2\tau_\alpha^2 [2\gamma_{ij} \gamma_{jk} + (1 + Z_\alpha)(\omega_{ij} \gamma_{jk} + \omega_{kj} \gamma_{ji})] \} , \end{aligned} \tag{3.34}$$

where

$$\begin{aligned} Z_\alpha = & \frac{2}{3} \gamma_\alpha , \quad \gamma_\alpha \ll 1 , \\ Z_\alpha = & \frac{4}{27} (9 - 42\gamma_\alpha^{-1} + 245\gamma_\alpha^{-2}) , \quad \gamma_\alpha \gg 1 . \end{aligned}$$

One may assume that  $Z$  is a monotonically increasing function of  $\gamma$  and if necessary may be fitted by any kind of convenient function.

We may note that, by virtue of the possible dependence  $\gamma$  on the velocity gradients mentioned above, the expressions for the moments are valid only to within second-order terms.

## 4. Viscoelasticity of dilute solutions

A dilute polymer solution may be represented as an assembly of macromolecular coils suspended in a viscous liquid, the stresses tensor of which assumes the following form on deformation:

$$\sigma_{ik}^0 = -p\delta_{ik} + 2\eta^0 \gamma_{ik} \tag{4.1}$$

and the problem involves primarily the calculation of the stresses tensor for a suspension of macromolecular coils.

### 4.1 The stress tensor

Suppose that  $n$  is the density of the number of coils. Since each macromolecule can be represented schematically by  $N + 1$  Brownian particles, a unit volume contains  $n(N + 1)$  Brownian particles—a number which is sufficiently large

to introduce macroscopic variables for the system of Brownian particles: the density

$$\rho(\mathbf{x}, t) = \sum m \langle \delta(\mathbf{x} - \mathbf{r}^\alpha) \rangle = m(N+1)n(\mathbf{x}, t) \quad (4.2)$$

and the density of the momentum

$$\rho v_j(\mathbf{x}, t) = \sum m \langle u_j^\alpha \delta(\mathbf{x} - \mathbf{r}^\alpha) \rangle. \quad (4.3)$$

In Eqns (4.2) and (4.3), the summation is carried out with respect to all the particles per unit volume and the average is with respect to the assembly of the realisations of the random force.

In order to determine the stress tensor for a moving system of Brownian particles, we shall consider, using the methods developed in the theory of liquids [31], the variation of the density of the momentum:

$$\begin{aligned} \frac{\partial}{\partial t} \rho v_j &= -\frac{\partial}{\partial x_i} \sum m \langle u_j^\alpha u_i^\alpha \delta(\mathbf{x} - \mathbf{r}^\alpha) \rangle \\ &+ \sum \left\langle m \frac{du_j^\alpha}{dt} \delta(\mathbf{x} - \mathbf{r}^\alpha) \right\rangle \end{aligned} \quad (4.4)$$

and shall formulate the right-hand side of this equation in a divergent form. In order to transform the second term into the required form, we shall make use of the equation for the dynamics of the macromolecule. Turning to Eqn (3.19), we multiply it by  $\delta(\mathbf{x} - \mathbf{r}^\alpha)$ , carrying out the summation with respect to all the particles of the macromolecule and averaging the result. We may note that the average force acting on the coil from the side of the liquid is zero, i.e. one must put

$$\sum_\alpha \langle (\mathbf{F}^\alpha + \Phi^\alpha) \delta(\mathbf{x} - \mathbf{r}^\alpha) \rangle = 0.$$

Thus for each coil we have

$$m \sum_\alpha \left\langle \frac{d\mathbf{u}^\alpha}{dt} \delta(\mathbf{x} - \mathbf{r}^\alpha) \right\rangle = \sum_\alpha \langle (\mathbf{K}^\alpha + \mathbf{G}^\alpha) \delta(\mathbf{x} - \mathbf{r}^\alpha) \rangle.$$

Next, we use the formal expansion of the  $\delta$ -function in Taylor's series about the coordinate of the centre of gravity of the  $\alpha$ th macromolecules  $\mathbf{q}^\alpha$ , retaining only two terms of the expansion:

$$\delta(\mathbf{x} - \mathbf{r}^\alpha) = \delta(\mathbf{x} - \mathbf{q}^\alpha) - (r_k^\alpha - q_k^\alpha) \frac{\partial}{\partial x_k} \delta(\mathbf{x} - \mathbf{q}^\alpha)$$

and we transform the formula written above into

$$-\frac{\partial}{\partial x_k} \sum_\alpha \langle (K_j^\alpha r_k^\alpha + G_j^\alpha r_k^\alpha) \delta(\mathbf{x} - \mathbf{q}^\alpha) \rangle.$$

In this relation, the summation is carried out with respect to the particles of one macromolecule. Carrying out the summation with respect to all the macromolecules and neglecting the statistical dependence of the coordinates of the centres of gravity of the macromolecular coils on the remaining coordinates, we obtain an expression for the second term in Eqn (4.4) in a divergent form:

$$\sum \left\langle m \frac{du_j^\alpha}{dt} \delta(\mathbf{x} - \mathbf{r}^\alpha) \right\rangle = -\frac{\partial}{\partial x_k} n \sum_\alpha \langle K_j^\alpha r_k^\alpha + G_j^\alpha r_k^\alpha \rangle.$$

Taking into account the assumptions made in this derivation, the expression for the second term in Eqn (4.4) must also be formulated in a more convenient

form. Using the equation for the average velocity and taking into account the first term of the expansion of the  $\delta$ -function, we find

$$m \sum \langle u_i^\alpha u_i^\alpha \delta(\mathbf{x} - \mathbf{q}^\alpha) \rangle = nm \sum_\alpha \langle (u_j^\alpha - v_j)(u_i^\alpha - v_i) \rangle + \rho v_i v_j.$$

The symbol indicating the derivative in the transformed right-hand side of Eqn (4.4) includes the expression for the flux of momentum, from which we subtract the convective transfer of momentum and find the stress tensor:

$$\sigma_{kj} = -n \sum_\alpha [m \langle (u_j^\alpha - v_j)(u_k^\alpha - v_k) \rangle + \langle K_k^\alpha r_j^\alpha + G_k^\alpha r_j^\alpha \rangle]. \quad (4.5)$$

One may assume that the local-equilibrium distribution with respect to velocities holds, which yields

$$\sigma_{jk} = -n(N+1)T\delta_{jk} + n \sum_\alpha \langle K_j^\alpha r_k^\alpha + G_j^\alpha r_k^\alpha \rangle. \quad (4.6)$$

The additional stresses defined by this formula arise owing to the difference between the rate of diffusion  $w^\alpha$  of the Brownian particle and the average velocity of the medium  $v^\alpha$  at the point where the particle is located. This leads to the appearance of bulk-phase forces, which can be written in the following form for slow motions:

$$\mathbf{F}^\alpha = -\zeta(v^\alpha - w^\alpha).$$

After averaging, the additional stresses assume the form

$$-n\zeta \sum \langle (v_i^\alpha - w_i^\alpha) r_k^\alpha \rangle,$$

where the angular brackets denote averaging with respect to the distribution function for the coordinates of all the particles. After determining the rate of diffusion, the expression formulated leads to the result indicated above.

Next it is convenient to go over to the normal coordinates defined by Eqn (2.12). After a special choice of the internal friction matrix, considered in the second Section, we have

$$\sigma_{ik} = -nT\delta_{ik} + n \sum_{v=1}^N [2\mu T \lambda_v \langle \rho_i^\alpha \rho_k^\alpha \rangle - T\delta_{ik} + \zeta \gamma_v \langle e_k^\alpha e_i^\alpha \rho_j^\alpha \rho_j^\alpha \rangle].$$

In the last term, one can carry out the averaging with respect to velocities and replace  $\rho_j^\alpha$  by the average velocity  $\psi_j^\alpha$ . Taking into account the fact that  $\langle e_k^\alpha e_i^\alpha \rho_j^\alpha \nabla_j \ln W \rangle = -3\langle e_i^\alpha e_k^\alpha \rangle$ , we find [28]

$$\begin{aligned} \sigma_{ik} &= -nT\delta_{ik} + \frac{1}{2}n\zeta \sum_{v=1}^N \left[ \frac{1}{\tau_v} \left( \langle \rho_i^\alpha \rho_k^\alpha \rangle - \frac{3}{2\mu\lambda_k} \langle e_i^\alpha e_k^\alpha \rangle \right) \right. \\ &\quad \left. + \frac{1}{\tau_v} \frac{3}{2\mu\lambda_\alpha} \left( \langle e_i^\alpha e_k^\alpha \rangle - \frac{1}{3}\delta_{ik} \right) + \frac{2\gamma_v}{1+\gamma_v} \langle \rho_k^\alpha \rho_i^\alpha e_j^\alpha e_s^\alpha \gamma_{js} \rangle \right], \end{aligned} \quad (4.7)$$

where the relaxation times  $\tau_v$  and  $\tau_v'$  were determined previously.

In order to determine the stress tensor for the entire system (a dilute solution of the polymer), the stresses in the solvent (a viscous liquid), defined by Eqn (4.1), must be added to Eqns (4.5)–(4.7) defining the stresses in a continuum of Brownian particles. The stress tensor for a dilute polymer solution is expressed in terms of moments—additional variables which were discussed in the previous Section. The system of equations for the moments in the case where the macromolecule is characterised by an internal viscosity, proves to be open. The first of the chain

of equations for the moments were presented previously [see Eqns (3.31) and (3.33)].

The expressions for the stress tensor (4.7) together with the equations for the moments, the continuity equations, and the equations of motion constitute the basis of the dynamics of dilute polymer solutions. This system of equations may be used to investigate the flow of dilute solutions in various experimental situations. Certain simple cases will be examined in the subsequent subsections of the present Section in order to demonstrate the applicability of the expressions obtained to dilute solutions, to indicate the region of their applicability, and to refine the expressions for the eigenvalues  $\gamma_v$ , which were introduced previously as phenomenological constants.

### 4.2 Characteristics of linear viscoelasticity

The study of the reaction of the system in the simple case where the velocity gradients are independent of the coordinates and vary in accordance with the law

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

for different deformation frequencies  $\omega$  yields important information about the relaxation processes in the system.

In this case, Eqn (4.7), combined with the expressions for the moments which can be calculated by Eqns (3.31) and (3.33), defines [28] the stress in a dilute solution of polymers in terms of a linear approximation.

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

where  $\eta(\omega)$  is the complex shear viscosity with the components

$$\begin{aligned} \eta'(\omega) &= \eta^0 + nT \sum_{v=1}^N \frac{\tau_v}{1 + \gamma_v} \\ &\times \frac{1}{5} \left[ 2\gamma_v + \frac{3(1 + \gamma_v)}{1 + (\tau_v\omega)^2} + \frac{2}{1 + (\tau'_v\omega)^2} \right], \\ \eta''(\omega) &= nT \sum_{v=1}^N \tau_v^2 \omega \cdot \frac{1}{5} \left[ \frac{3}{1 + (\tau_v\omega)^2} + \frac{2}{1 + (\tau'_v\omega)^2} \right]. \end{aligned} \quad (4.8)$$

Since the velocity gradient is related to the displacement gradient by the expression  $v_{12} = -i\omega\lambda_{12}$ , it follows that, instead of the dynamic viscosity, use may be made of another characteristic—the dynamic modulus. The components of the above complex quantities are linked by the relation

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

In the study of the linear response, it is convenient to consider quantities independent of the concentration and viscosity—the characteristic [intrinsic] viscosity and the characteristic modulus:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta^0}{\eta^0 c}, \quad [G] = \lim_{c \rightarrow 0} \frac{G - i\eta^0\omega}{nT}, \quad (4.9)$$

$\eta^0$  is the viscosity of the solvent and  $c = nMN_A^{-1}$  the weight concentration of the polymer ( $N_A =$  Avogadro number).

Fig. 3 illustrates the dependence of the characteristic viscosity as defined by Eqn (4.8) on the dimensionless frequency  $\tau_1\omega$  for different theoretical parameters, which appeared in the formulae for the dependence of the intramolecular friction coefficient and the dependence of

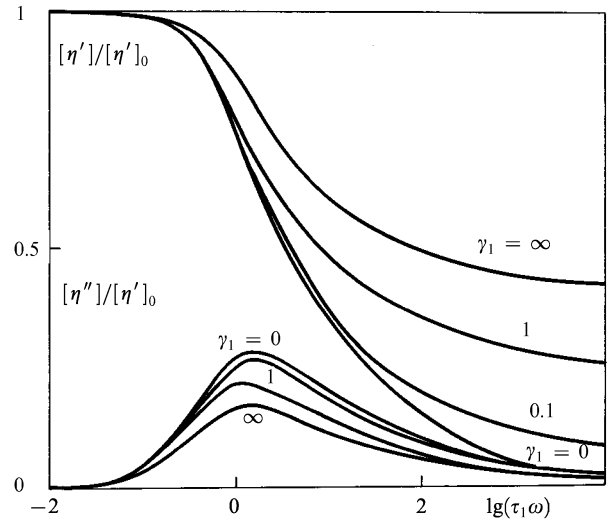


Figure 3. Dependence of the real (upper curves) and imaginary (lower curves) components of the shear viscosity on the dimensionless frequency for an impermeable ( $z\nu = 1.5, \Theta = 0.5$ ) coil. The numbers opposite the curves denote the internal viscosity  $\gamma_1$ .

the relaxation times introduced previously on the number of the mode:

$$\begin{aligned} \tau_\alpha &= \tau_1 \alpha^{-z\nu}, & \tau'_\alpha &= \tau_\alpha (1 + \gamma_\alpha), \\ \gamma_\alpha &= \gamma_1 \alpha^\Theta, & \alpha &= 1, 2, \dots \ll N. \end{aligned}$$

The exponents in the above expressions can be estimated beforehand from the dependence of the limiting values of the characteristic viscosity at low and high frequencies on the length of the macromolecule:

$$[\eta']_0 = \frac{nT}{c\eta^0} \sum_\alpha \tau_\alpha \sim M^{z\nu-1}, \quad (4.10)$$

$$[\eta']_\infty = \frac{2nT}{5c\eta^0} \sum_\alpha \frac{\tau_\alpha \gamma_\alpha}{1 + \gamma_\alpha} \sim M^{z\nu-1-\Theta}. \quad (4.11)$$

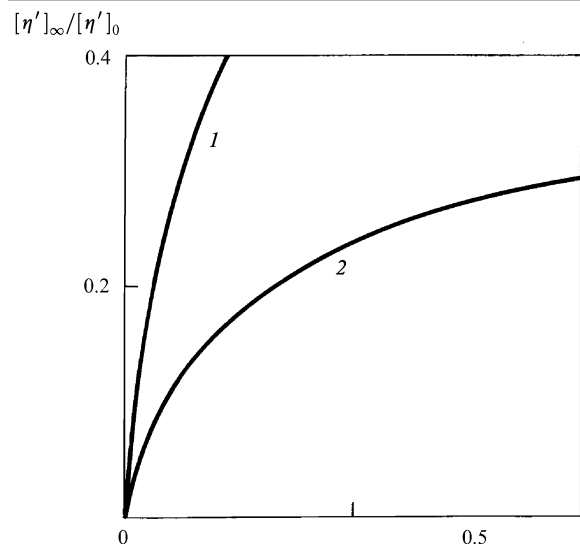


Figure 4. Dependence of the ratio of the limiting characteristic viscosities on the internal rigidity coefficient of the macromolecular coil for the parameters ( $z\nu = 1.5$  and  $\Theta = 0.5$  on the basis of the theories of Peterlin [32] (curve 1) and Pokrovskii and Tonkikh [28] (curve 2).

We may note that the case where  $\gamma_1 = 0$  and  $zv = 2$ , corresponding to an ideally flexible permeable macromolecule, reproduces the relations indicated by Rouse [4]. For low internal viscosities  $\gamma$ , the results found by Peterlin [32] follow from Eqns (4.8). The results for an arbitrary internal viscosity have been published [28]. Fig. 4 presents a comparison of the results. The infinite ratios of the limiting values demonstrate the inadequacy of Peterlin's theory in the region of high internal viscosities.

### 4.3 Initial characteristic viscosity

The characteristic viscosity at low frequencies makes it possible to estimate the role of the volume effects and of the hydrodynamic interaction in the dynamics of the macromolecule, which influence, according to Eqn (4.10), the dependence of the quantity under discussion on the molecular weight (the length of the macromolecule)

$$[\eta']_0 = KM^{zv-1}. \quad (4.12)$$

Theoretical estimates of the quantity  $zv - 1$  (Table 1) are in the range from 0.5 (impermeable Gaussian coil), to 1.11 (permeable coil with bulk-phase interaction). A compilation of empirical values of  $K$  and of the power exponents for different polymers and different solvents may be found in the literature [8, 15]. Some of the values are presented in Table 2. The empirical values of the exponent  $zv - 1$  do not exceed 0.9, which indicates a significant impermeability of the macromolecular coil in a flow.

**Table 2.** The constants in Eqn (4.12).

Polymer	Solvent	Temperature/°C	$10^4 K / \text{dl g}^{-1}$	$zv - 1$
Polystyrene	Benzene	25	0.42	0.774
"	Cyclohexane	35	8.4	0.5
Poly(methylmethacrylate)	Chloroform	25	0.34	0.83
Polyisobutylene	Toluene	25	8.7	0.56
"	Benzene	24	10.7	0.5
Polybutadiene	Cyclohexane	20	360	0.70
Polyisoprene (natural rubber)	"	20	300	0.7
Polymethylsiloxane	Toluene	25	73.6	0.72
"	Bromocyclohexane	28	5.6	0.5

For an impermeable coil, the characteristic viscosity defined by Eqn (4.10) can be expressed in the form

$$[\eta]_0 = \Phi \frac{\langle S^2 \rangle^{3/2}}{M}, \quad (4.13)$$

where  $\langle S^2 \rangle$  is the average square of the radius of inertia of the coil, while the experimental value of the constant  $\Phi$ , called the Flory constant, is [8]

$$\Phi = 2.66(\pm 0.1) \times 10^{23} \text{ mol}^{-1}.$$

A study of the characteristic viscosity defined by Eqn (4.13) makes it possible in this case to interpret a dilute solution of macromolecules as a suspension of solid nondeformable spheres with a radius close to the mean square radius of inertia.

The initial characteristic viscosity defined by Eqn (4.10) is independent of the characteristics of the intramolecular

friction, but this is a consequence of simplifying assumptions. It has been shown for a dumbbell [2] that, when account is taken simultaneously of the internal viscosity and the anisotropy of the hydrodynamic interaction, then the characteristics of these quantities enter into the expression for the viscosity of type (4.10). This result must appear also for the subchains model when account is taken of the anisotropy of the hydrodynamic interaction. Once a relation of type (4.11) has been established for a certain polymer, it can be used to determine the molecular weight of the polymer from the characteristic viscosity [15].

### 4.4 The mechanism of the intramolecular viscosity

The limiting characteristic viscosity, defined by Eqn (4.11), is of special interest in the study of the influence of intramolecular friction on the dynamics of the macromolecule in a viscous liquid. For low initial characteristic viscosities  $\gamma \ll 1$ , Eqn (4.11) can be rewritten thus:

$$[\eta']_\infty = \frac{2}{5} \frac{nT}{c\eta^0} \zeta(zv - \Theta) \tau_1 \gamma_1, \quad (4.14)$$

where  $\zeta(x)$  is Riemann's zeta-function.

Experimental studies indicate [33, 34] that the limiting characteristic viscosity for a given polymer-homologous series is independent of the length of the macromolecule and the type of solvent.

Since  $\tau_1 \sim M^{zv}$ ,  $n \sim M^{-1}$ , and  $\gamma_1 \sim M^{-\Theta}$ , the relation

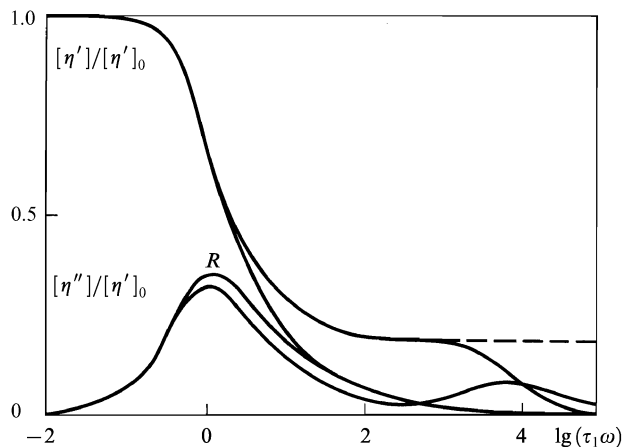
$$\Theta - zv + 1 = 0. \quad (4.15)$$

follows from Eqn (4.14) and the fact that the limiting characteristic viscosity is independent of the length of the macromolecule.

A consequence of the independence of the limiting characteristic viscosity of the type of solvent is that  $\gamma_1$  is independent of the viscosity of the solvent, which means that the dimensional characteristic of the 'internal' friction of the macromolecule  $\zeta\gamma_1$  is proportional to the viscosity of the solvent and the 'internal' friction is not solely internal. On the basis of empirical studies, the conclusion that the solvent contributes significantly to the intramolecular viscosity was reported recently [35] and was referred to as the 'solvent modification effect'.

The fact that the limiting value of the characteristic viscosity at high frequencies is not zero indicates the existence of intramolecular (taking into account the solvent molecules) relaxation processes with relaxation times which are smaller than the reciprocal of the frequency of the measurement. The true limiting value is naturally zero and experiment sometimes reveals a step at a frequency  $\omega_s$ , which indicates the occurrence of a relaxation process with a relaxation time  $\tau \sim \omega_s^{-1}$ . This phenomenon may be described by including the relaxing intramolecular viscosity [27].

Fig. 5 illustrates the dependence of the viscosity on the frequency obtained taking into account the intramolecular relaxation process with a relaxation time  $\tau$ . It may be hoped that the study of intramolecular relaxation processes from a phenomenological point of view will promote the establishment of the detailed mechanism of the rapid relaxation processes in polymers, although there is no doubt that more detailed models of the macromolecule must be used at high frequencies.



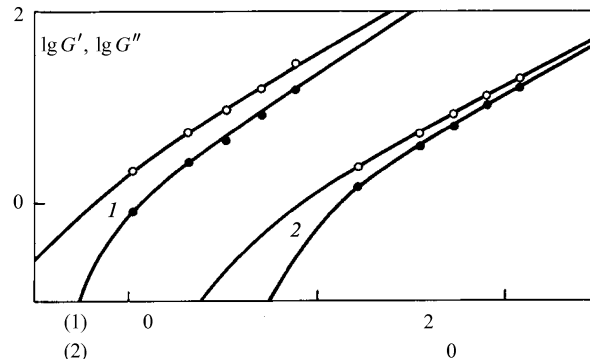
**Figure 5.** Dependence of the real and imaginary components of the characteristic viscosity on the dimensionless frequency. The curves have been calculated for  $\gamma_1 = 0.1$  and  $\tau/2\tau_1 = 10^{-5}$ . The dashed line represents the continuation of the relation based on Peterlin's theory [32]. The curves designated by the letter *R* represent the dependence based on Rouse's theory ( $z\nu = 2, \Theta = 0$ ).

### 4.5 The dynamic modulus

Here comparison will be made of the values of the characteristic modulus calculated by Eqns (4.8)–(4.9) with the corresponding experimental values.

Fig. 6 demonstrates that, for certain values of the maximum relaxation time  $\tau_1$  and certain values of the exponents  $z\nu$  and  $\Theta$ , the theory reproduces satisfactorily the experimental relations for polymer solutions at infinite dilution [36–39].

We may note yet again that the identifying constants are unambiguously determined by the limiting values of the characteristic viscosity and can be estimated independently, so that one may conclude that, in the region of comparatively low frequencies, the schematic representation of the macromolecule by a subchain taking into account intramolecular friction, the volume effects, and the hydrodynamic interaction makes it possible to explain the dependence of the viscoelastic behaviour of dilute polymer solutions on the molecular weight, temperature, and frequency. At low frequencies, the description becomes universal. In order to describe the dependence of the dynamic modulus on the frequency at high values of the latter, use must be made of other more detailed models,



**Figure 6.** Dependence of the characteristic dynamic modulus for polystyrene solutions in decalin (curve 1) and in toluene (curve 2) on the frequency. Circles—experimental values according to Russer et al. [39]. The theoretical curves have been plotted for  $z\nu = 1.788$  and  $\tau_1 = 2.5 \times 10^{-3}$  s for case 1 and  $z\nu = 1.5$  and  $\tau_1 = 8.35 \times 10^{-4}$  for case 2.

which have been examined, for example by Gotlib et al. [5] and Priss and coworkers [40, 41], and which make it possible to describe large-scale motions of the chain.

As an illustration, certain data characterising dilute polymer solutions are presented in Table 3.

### 4.6 Nonlinear effects in simple shear

The hypothesis, employed in the theory, that certain true values can be replaced by average equilibrium values renders the results applicable for small extensions of the macromolecular coil and hence for low velocity gradients: the results for the moments are valid to within second-order terms in the velocity gradients. It follows from Eqns (3.31) and (4.7) that, for low velocity gradients in the stationary case the expression for the stress tensor is

$$\sigma_{ik} = -p\delta_{ik} + 2\eta^0\gamma_{ik} + \frac{1}{2}n\zeta \sum_{\nu=1}^N (v_{ij}\langle\rho_j^\nu\rho_k^\nu\rangle + v_{kj}\langle\rho_j^\nu\rho_i^\nu\rangle). \quad (4.16)$$

This equation makes it possible to calculate stresses to within third-order terms in the velocity gradient.

We shall consider the case of shear when one of the components of the velocity gradient tensor has been specified and is constant, namely  $v_{12} \neq 0$ . This case is close to the situations which as a rule occur in the experimental study of polymer solutions [15]. In order to achieve such a flow, it is necessary in this case that stresses

**Table 3.** The characteristic viscosities and maximum relaxation times of dilute solutions.

System	$T/^\circ\text{C}$	$\rho^0/\text{g cm}^{-3}$	$\eta^0/\text{P}$	$10^{-5}/M$	$[\eta]/\text{cm}^3 \text{g}^{-1}$	$10^4 \tau_1/\text{s}$
Polystyrene in decalin [36]	16	0.8868	0.0295	8.6	76	0.35
Polystyrene in di-2-ethyl-hexyl phthalate [36]	22	0.9827	0.678	8.6	—	7.59
Polystyrene in $\alpha$ -chloronaphthalene [36]	25	1.195	0.0315	8.6	197	1.26
Polystyrene in apochlor 1232 [36]	25	1.269	0.142	8.6	183	3.98
"	25	1.269	0.142	4.1	111	1.2
1,4-Polybutadiene in chloronaphthalene [37]	25	—	0.0312	2.2	200	0.26
"	25	—	0.0312	9.1	510	2.75
1,4-Polybutadiene in decalin [37]	25	—	0.0245	9.1	510	2.14
Poly- $\alpha$ -methylstyrene in $\alpha$ -chloronaphthalene [38]	25	—	0.0315	14.3	252	2.0
Poly- $\alpha$ -methylstyrene in decalin [38]	25	—	0.0245	14.3	135	0.79
Polystyrene in decalin [39]	15	0.887	0.287	180	300	23
Polystyrene in toluene [39]	20	0.867	0.0059	180	3100	69

should be applied to the system and not only the shear stress  $\sigma_{12}$ , as in the case of a linear viscous liquid, but also normal stresses, so that in the case under consideration the stresses tensor is

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}.$$

The shear stress  $\sigma_{12}$  and the differences between the normal stresses  $\sigma_{11} - \sigma_{33}$  and  $\sigma_{22} - \sigma_{33}$  are usually measured in the experiment.

For a specified motion, Eqn (4.16) defines, apart from the second-order moments (3.34), the nonzero components of the stress tensor, which makes it possible to formulate the expressions for the shear viscosity and the difference between the normal stresses:

$$\eta = nT \sum_{v=1}^N \tau_v \left[ 1 - Z_v (\tau_v v_{12})^2 \right], \quad (4.17)$$

$$\sigma_{11} - \sigma_{33} = nT \sum_{v=1}^N (\tau_v v_{12})^2, \quad \sigma_{22} - \sigma_{33} = 0. \quad (4.18)$$

It follows from Eqns (4.17) that the viscosity or, what amounts to the same thing, the characteristic viscosity is independent of the velocity gradient for flexible chains ( $\gamma_1 = 0$ ). For chains with an internal viscosity, the viscosity diminishes with increase in the velocity gradient. The nature of the variation may be estimated. It is readily seen from Eqns (3.34) that, for high values of  $\gamma_v$ ,  $Z_v$  does not exceed 4/3 and therefore only the first terms contribute to the sum in Eqn (4.17), which includes  $Z_v$ , and for high molecular weights one can therefore assume that

$$Z_v \sim \gamma_v = \gamma_1 v^\Theta, \quad \Theta > 0, \quad \gamma_1 \sim M^{-\Theta}.$$

From Eqn (4.15), according to which  $\Theta = z_v - 1$ , the dependence of the viscosity defined by Eqn (4.17) on the molecular weight can be formulated as follows:

$$\eta - \eta_0 \sim M^{2z_v} v_{12}^2. \quad (4.19)$$

According to the theoretical estimate of the exponent (Table 1),  $z_v$  varies from 1.5 (impermeable Gaussian coil) to 2.11 (permeable coil with bulk-phase interactions). Empirical estimates of the exponent  $z_v$  by Eqn (4.19) for solutions in which the coils are nearly unperturbed yield the exponent  $2z_v \approx 3$  [15, 42].

We may note that it has been shown for the dumbbell [2] that the joint allowance for the internal viscosity and the anisotropy of the hydrodynamic interaction leads to the appearance of a nonzero second difference between the normal stresses  $\sigma_{22} - \sigma_{33}$ . Since the internal viscosity may be estimated, for example, from dynamic measurements, this effect may serve for the estimation of the anisotropy of the hydrodynamic interaction in a molecular coil.

## 5. Optical anisotropy

Polymers and their solutions become optically anisotropic in a flow, which is associated with the fact that the optically anisotropic parts of the macromolecule (units and segments) are oriented by the flow and the entire macromolecular coil is deformed in the latter. This

phenomenon is widely used in combination with theoretical results for the investigation of the structures and properties of macromolecules [15].

### 5.1 The relative permittivity tensor

In order to examine the optical anisotropy, we begin with the relative permittivity tensor for the system  $\varepsilon_{ik}$ , which is defined (see e.g. Landau and Lifshits [43]) by the relation

$$\varepsilon_{ik} E_k = E_i + 4\pi P_i, \quad (5.1)$$

where  $E_k$  is the average electric field strength acting in the medium and  $P_i$  is the polarisation per unit volume of the system expressed in terms of the polarisabilities of the constituent elements of the system.

We shall make use of the heuristic model mentioned previously in Section 2.1: each macromolecule consists of  $z$  segments and is surrounded by solvent molecules. Suppose that the solvent molecules have an isotropic polarisability  $\alpha_0$ , while the segment has an anisotropic polarisability  $\alpha_{ik}$ . In the coordinate system linked to the segment, the anisotropy tensor is diagonal and we assume that it has axial symmetry, so that  $\alpha_{22} = \alpha_{33}$ . In any other coordinate system, the polarisability tensor of the segment has the form

$$\alpha_{ik} = c_{is} c_{ks} \alpha_{ss},$$

where  $c_{is}$  is the cosine of the angle between the  $i$ th axis of the laboratory system and the  $s$ th axis of the molecule.

Each solvent molecule makes an isotropic contribution to the polarisability vector; the contribution of each segment of the macromolecule is anisotropic and is expressed by the formula

$$\beta_s = c_{si} c_{ki} \alpha_{ii} F_k = \left[ \alpha \delta_{sk} + \Delta \alpha \left( c_{s1} c_{k1} - \frac{1}{3} \delta_{sk} \right) \right] F_k,$$

where  $\alpha = (\alpha_{11} + 2\alpha_{22})/3$  and  $\Delta \alpha = \alpha_{11} - \alpha_{22}$ .

The true molecular field  $F$  acting on the segment differs from the average field  $E$  because the scale of the dimensions of the segments is molecular.

Taking into account all the molecules and segments and designating by  $nz$  and  $m$  the densities of the number of segments and of the number of solvent molecules ( $n$  is the density of the number of macromolecules), we obtain, after averaging with respect to the orientations of the segments,

$$P_s = (nz \alpha \delta_{sk} + nz \Delta \alpha a_{sk} + m \alpha_0 \delta_{sk}) F_k, \quad (5.2)$$

where a symbol has been introduced for the average of the directing cosines for the segment relative to the laboratory coordinate system—the orientation tensor  $a_{sk} = \langle c_{s1} c_{k1} \rangle - \delta_{sk}/3$ . The internal field  $F_k$  is assumed to be the same for the segments and solvent molecules.

Next, use is made of the simple hypothesis that all the positions of the molecules and segments are equally probable, so that, following tradition [44], we formulate an expression for the internal field as a field within a spherical cavity:

$$F_i = E_i + \frac{4\pi}{3} P_i. \quad (5.3)$$

Eqns (5.1)–(5.3) define the relative permittivity tensor for the system which is formulated below to within second-order terms in the orientation tensor:

$$\begin{aligned} \varepsilon_{ik} = & \varepsilon_0 \delta_{ik} + 4\pi n z \Delta\alpha \left( \frac{\varepsilon_0 + 2}{3} \right)^2 a_{ik} \\ & + \frac{1}{2} \left[ 1 - \varepsilon_0 + 4\pi \left( \frac{\varepsilon_0 + 2}{3} \right)^3 \right] (4\pi n z \Delta\alpha)^2 \left( \frac{\varepsilon_0 + 2}{3} \right)^2 \\ & \times a_{jl} a_{lj} \delta_{ik} + \frac{1}{3} (4\pi n z \Delta\alpha)^2 \left( \frac{\varepsilon_0 + 2}{3} \right)^3 a_{il} a_{lk} . \end{aligned} \quad (5.4)$$

To a first approximation, allowance for the internal field by the Lorentz procedure is equivalent to multiplication by the factor

$$\left( \frac{\varepsilon_0 + 2}{3} \right)^2 .$$

This result is well known [44] for isotropic systems. In the second approximation, the principal axes of the relative permittivity tensor do not coincide, generally speaking, with the principal axes of the orientation tensor.

In conformity with the significance of the terms employed by investigators of anisotropy [15], the effects associated with the first-order terms in Eqn (5.4) may be called the effects of the intrinsic anisotropy, while the second-order effects may be referred to as the effects of the anisotropy of the microform. It is readily seen that interesting situations may arise when  $\Delta\alpha < 0$ ; in this case, the coefficients of the first- and second-order terms have different signs.

## 5.2 The polarisability of the macromolecular coil

Eqn (5.4), formulated in the previous Section, defines the relative permittivity tensor in terms of the average orientation of certain uniformly distributed anisotropic elements, which we shall interpret here as the Kuhn segments of the model of the macromolecule described in Section 2.1 and we shall now discuss the characteristic features arising on passing to the consideration of a dilute polymer solution, in which the segments of the macromolecule are not uniformly distributed but are concentrated in the macromolecular coils.

As before, we consider each macromolecule to be divided into  $N$  subchains and, using the formula relating the tensor of the average orientation of the segments of the macromolecules  $a_{jk}$  to the distance between the ends of the chain [6–8], we arrive, to a first approximation on the basis of Eqn (5.4), at Zimm's expression [45] for the relative permittivity tensor:

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} + n\Gamma \left( \langle r_i^\alpha A_{xy} r_j^\beta \rangle - \frac{1}{3} \langle r_j^\alpha A_{xy} r_j^\beta \rangle \delta_{ik} \right) , \quad (5.5)$$

where  $n$  is the density of the number of macromolecules in solution, the matrix  $A$  has the form specified by formula (2.8), while the coefficient of the anisotropy of the macromolecular coil  $\Gamma$  is given by the following expression in the case where the macromolecule is modelled by a freely jointed chain of Kuhn segments:

$$\Gamma = 4\pi\Delta\alpha \left( \frac{\varepsilon_0 + 2}{3} \right)^2 \frac{3N}{5z l^2} ,$$

where  $z$  is the number of Kuhn segments in the macromolecule.

The anisotropy of the macromolecule has been calculated for other chain models. Expressions are known for the anisotropy coefficient in the case where the macromolecule has been represented schematically by a continuous fila-

ment (the persistent length model) [46, 47] and also in the case where the microstructure of the macromolecule has been specified. In the latter case, the anisotropy coefficient of the macromolecule is expressed in terms of the bond polarisabilities and other microcharacteristics of the macromolecule [6–8].

The expression for the relative permittivity tensor [Eqn (5.5)] in terms of the normal coordinates introduced by means of Eqns (2.12), assumes the form

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} + n\Gamma \sum_{\alpha=1}^N \lambda_\alpha \left( \langle \rho_i^\alpha \rho_k^\alpha \rangle - \frac{1}{3} \langle \rho_j^\alpha \rho_j^\alpha \rangle \delta_{ik} \right) . \quad (5.6)$$

When account is taken of the excluded volume effects, one must also take into account the possible effect of the shielding of the inner segments of the macromolecular coil, the latter effect being greater the longer the macromolecule, so that the expression for the anisotropy coefficient, which is covariant in relation to the subdivisions into subchains, assumes the form

$$\Gamma = 4\pi\Delta\alpha \left( \frac{\varepsilon_0 + 2}{3} \right)^2 \frac{3N^{2\nu}}{5\langle R^2 \rangle} . \quad (5.7)$$

The dependence of the polarisability coefficient on the length of the macromolecule may deviate from the relation which follows from Eqn (5.7).

$$\Gamma \sim M^{-2\nu} . \quad (5.8)$$

The expression for the relative permittivity tensor [Eqn (5.6)] is valid only to a first approximation as regards the orientations of the segments and describes, in words of Tsvetkov et al. [15], the anisotropy of the system associated with the intrinsic anisotropy of the segments. In order to take into account the anisotropy of the microform, one must turn to the second-order terms in Eqn (5.4).

The expressions given above are valid for polymer solutions at any concentration and are independent of the assumptions made in the calculation of the moments. Here it only remains to use the expressions for the moments in order to obtain the dependence of the relative permittivity tensor on the velocity gradients.

## 5.3 Anisotropy in a stationary shear flow

The expressions for the relative permittivity tensor [Eqn (5.6)] are valid for flows of arbitrary type. However, the optical anisotropy of polymer systems is frequently studied [15] under the conditions of simple shear when the velocity gradient  $v_{12} \neq 0$ . The system investigated then becomes, generally speaking, a 'triaxial dielectric crystal' with nonzero components of the relative permittivity tensor.

The relative permittivity tensor is then nondiagonal but can be brought to the diagonal form by rotation about axis 3 by an angle  $\chi$  defined by the formula

$$\tan 2\chi = \frac{2\varepsilon_{12}}{\varepsilon_{11} - \varepsilon_{22}} . \quad (5.9)$$

The extinction angle  $\chi$  and the differences between the refractive indices (the extent of double refraction) in different principal directions are determined experimentally. For a beam propagated in directions 3 and 1, we find respectively

$$\begin{aligned} n_1 - n_2 &= \frac{1}{2\bar{n}} [(\varepsilon_{11} - \varepsilon_{22})^2 + 4\varepsilon_{12}^2]^{1/2}, \\ n_2 - n_3 &= \frac{1}{2\bar{n}} (\varepsilon_{22} - \varepsilon_{33}), \end{aligned} \quad (5.10)$$

where  $\bar{n}$  is the average refractive index.

We can now formulate on the basis of Eqn (5.6) the components of the relative permittivity tensor using the expressions for the moments [Eqn (3.34)] and can determine the gradient dependence of the above quantities to within second-order terms:

$$\begin{aligned} n_1 - n_2 &= S \sum_{v=1}^N \tau_v v_{12}, \\ n_2 - n_3 &= -S \sum_{v=1}^N Z_v (\tau_v v_{12})^2, \\ \tan 2\chi &= \frac{1}{2A v_{12}}, \quad \chi = \frac{\pi}{4} - A v_{12}, \end{aligned} \quad (5.11)$$

where the dimensionless quantity

$$S = \frac{n\Gamma}{2\bar{n}\mu} \sim M^{-1}. \quad (5.12)$$

independent of the number of subdivisions, has been introduced.

In order to establish the dependence of this quantity on the length of the macromolecule, one can determine experimentally the influence of the shielding effect.

The quantity

$$A = \frac{1}{2} \frac{\sum_v (1 + Z_v) \tau_v^2}{\sum_v \tau_v},$$

called the characteristic angle [15], has also been introduced in Eqns (5.11).

For low internal viscosities, the relation  $Z_v = (2/5)\gamma_v$  is valid, so that, knowing the dependence of the relaxation time and of the internal viscosity on the number of the mode, we can write, with the aid of the zeta-function  $\zeta(x)$ ,

$$A = \frac{1}{2} \frac{\tau_1}{\zeta(zv)} \left[ \zeta(2zv) + \frac{2}{5} \gamma_1 \zeta(2zv - \Theta) \right].$$

The first term is proportional to the solvent viscosity  $\eta^0$  and the second to the internal viscosity (kinetic rigidity) of the macromolecule, so that measurement of the anisotropy of solutions in different solvents makes it possible to estimate the quantity

$$\tau_1 \gamma_1 \sim M^{zv - \Theta}. \quad (5.13)$$

When account is taken of the relation indicated previously [see Eqn (4.15)], the power exponent in Eqn (5.13) is unity, which agrees with the experimental results [15, 48]

$$\tau_1 \gamma_1 \sim M^{1 \text{ to } 1.2}.$$

We may note that, for high velocity gradients in an experiment with  $\Gamma < 0$ , the so-called anomalous dependences of the degree of double refraction and of the extinction angle on the velocity gradient are observed [49–51], indicating that the principal axes of the tensor of the average orientation of the optical anisotropy do not

coincide. In order to interpret this phenomenon, one must turn in the first place to equations of type (5.4) for the relative permittivity tensor which are nonlinear as regards orientation.

#### 5.4 Oscillating double refraction

The consideration of the optical anisotropy for an oscillating velocity gradient  $\gamma_{ik} \sim e^{-i\omega t}$  is usually restricted [52] to a linear approximation. The relative permittivity tensor can then be expressed in the form

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} - 2\bar{n}S(\omega)\gamma_{ik}, \quad (5.14)$$

where a complex dynamo-optical coefficient  $S(\omega) = S'(\omega) + S''(\omega)$ , characterising the behaviour of the system, has been introduced.

Under the conditions of shear motion, Eqns (5.9) and (5.10) lead to the following quantities in the case considered.

$$\chi = \frac{\pi}{4}, \quad \Delta n = n_1 - n_2 = -S(\omega)v_{12}, \quad n_2 - n_3 = 0.$$

An expression for the dynamo-optical coefficients with components

$$\begin{aligned} S'(\omega) &= S \sum_{\alpha=1}^N \tau_{\alpha} \times \frac{1}{5} \left[ \frac{3}{1 + (\tau_{\alpha}\omega)^2} + \frac{2}{1 + (\tau'_{\alpha}\omega)^2} \right], \\ S''(\omega) &= S \sum_{\alpha=1}^N \tau_{\alpha}^2 \omega \times \frac{1}{5} \left[ \frac{3}{1 + (\tau_{\alpha}\omega)^2} + \frac{2(1 + \gamma_{\alpha})}{1 + (\tau'_{\alpha}\omega)^2} \right] \end{aligned} \quad (5.15)$$

follows from the expression for the relative permittivity tensor (5.6) and Eqn (3.31) for the moments. The quantity  $S$  is defined by Eqn (5.12).

In the case where the intramolecular viscosity is neglected ( $\gamma_1 = 0$ ), the frequency dependence of the dynamo-optical coefficient agrees with the analogous dependence of the shear viscosity [see Eqn (4.8) and Fig. 3]. When the intramolecular viscosity is taken into account ( $\gamma_1 \neq 0$ ), the variations of the dynamo-optical coefficient also remain similar to the relations shown in Fig. 3 except that the limit of the real part of the dynamo-optical coefficient at high frequencies is zero. By comparing these two quantities we can estimate from experimental data the importance of intramolecular friction in the dynamics of the macromolecule.

The frequency dependences of the dynamo-optical coefficient for infinitely dilute solutions are available in the literature [55] and it is interesting to compare them with the relations based on Eqns (5.15).

The theoretical results presented here [53] extend the results of Thurston and Peterlin [54] to the more general case where the bulk-phase interactions are taken into account and the internal viscosity parameters assume arbitrary values.

## 6. Conclusions

Dilute polymer solutions constitute a unique example of a system with slow relaxation processes. The study of this system demonstrates the importance for the description of the behaviour of a system, of the concept of the internal thermodynamic variable introduced in the thermodynamics of irreversible processes.



As already mentioned in the Introduction, the results presented are valid for solutions at limiting concentrations of the polymer ( $c \rightarrow 0$ ) and for cases where the solvent is a viscous liquid, i.e. when relaxation processes in the solvent are neglected, which is possible if the solvent relaxation time  $\tau$  is short compared with the characteristic relaxation time of the macromolecule:

$$\tau \ll \tau_1 .$$

The case where the characteristic times  $\tau$  of the external and internal resistance are comparable to the relaxation times of the macromolecule are of theoretical interest (for  $\tau = 0$ , one is concerned with the viscosity of the solvent and the intramolecular viscosity).

A problem of this kind arises in the study of the dynamics of the macromolecule in a nondilute system. A natural basis for the investigation of this problem is provided by the procedures of the non-Markov random processes, the use of which leads to unexpected and interesting results, which have been discussed in a review [56]. Thus it was found that, in contrast to the case examined in the present review, the existence of several relaxation branches follows from the general equation for the dynamics of the macromolecule and different phenomena are determined by different sets of relaxation branches. When viscoelastic behaviour is considered, it is found that the calculated principal relaxation time for the reaction of the system agrees with the initial specified relaxation time for the external and internal resistances or, in other words, the theory of viscoelasticity proves self-consistent with respect to the relaxation time.

When the thermal motion of the macromolecule is considered, a certain intermediate length  $\xi$  appears. The length is such that the nature of the displacement of the macromolecule and of its constituent particles is inconstant: for shifts by distances  $l < \xi$ , the motion is freer and the diffusion coefficient is smaller than for shifts by distances  $l > \xi$ . The macromolecule is found to be located near its initial position. This feature of the thermal motion of the macromolecule in a system of intertwined, weakly connected macromolecules was postulated by earlier investigators [57] and was described qualitatively by the introduction of a 'tube' with a radius  $\xi$  within which the macromolecule is able to execute the so-called reptation motions.

The study of the dynamics of the macromolecule on the basis of the generalised equation taking into account the character of external and internal resistances, which are in the nature of an after-effect, has led to the creation of a logical theory of the dynamic behaviour of concentrated polymer solutions at limiting concentrations ( $c \rightarrow 1$ ).

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