Translated from *Uspekhi Khimii* **58** 1746–1762 (1989) U.D.C. 541(64+24):539.199:532.72

Self-diffusion in solutions and melts of flexible-chain polymers

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ABSTRACT. The review deals with the characteristic features of the molecular motion of flexible chain macromolecules and oligomers associated with the multisegmental nature of the chain and topological limitations. The dependence of the self-diffusion coefficients of chain molecules in polymer melts and solutions, including a weakly cross-linked gel, is analysed. Attention is concentrated on data for self-diffusion where there is a change not only in the molecular weight (MW) of the diffusing molecule but also in the molecular weight of the macromolecules surrounding the specified molecule. Both model ideas and approaches based on the scaling theory, including the concept of the curvature of the trajectories of the "reptation tube", are used for the theoretical analysis. The "inhomogeneity" of the segmental mobility in the chain has made it possible to describe specific features of the behaviour of oligomers. The dependence of the self-diffusion coefficient on the MW of the chain and the matrix and on the concentration in the region of dilute, moderately concentrated, and concentrated solutions and melts has also been described quantitatively.

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I. Introduction

The problems of molecular mobility in polymeric materials have continually attracted the attention of both theoreticians and specialists in applied chemistry. Self-diffusion processes occupy a major place in this problem. Firstly, the principal features and characteristics of the mobility in polymeric materials are manifested most clearly in self-diffusion phenomena. Secondly, together with the chemical potential gradient, self-diffusion coefficients determine the rate of mass transfer in polymeric bodies. Thirdly, self-diffusion processes can affect significantly the rates of chemical reactions (diffusion-controlled chemical reactions). Despite the importance of the problem under discussion, these questions have not been solved appropriately because of the difficulty of experimental measurement of the self-diffusion coefficients (D) of chain molecules.

Together with further improvement of the "tracer" atom and NMR "spin echo" methods,[1,2] during the last ten years there has been a development of other methods for the investigation of self-diffusion processes based on the use of the laser technique.[3–5] The results of studies of self-diffusion processes up to 1983 have been surveyed in two books.[1,2] However, in recent years fundamentally new experimental data have been obtained for the mobility of polymers and theoretical equations describing satisfactorily the experimental behaviour have been proposed. Indeed, previously it was believed that the scaling theory is adequate for the understanding of the concentration dependence of D.[6] However, in the latest studies (see below) it was found that the predicted relations hold only over a limited concentration range. The predictions of the scaling theory concerning the dependence of D on the molecular weight M also failed to come true. Indeed, the scaling theory predicted a broken line (with a jump at a certain concentration) dependence of D on M. However, it has been shown in studies carried out in 1984–1986 that these results of the scaling theory are applicable only within a restricted concentration range. There are data which cannot be in any way reconciled with the previously proposed theoretical relations.

The aim of the present study is the analysis of both experimental and theoretical results for the self-diffusion coefficients of macromolecules, obtained mainly in recent years, and the establishment of a correlation of these results with one another.

II. Characteristic features of the molecular motion of flexible chain polymers

The characteristic features of the molecular motion of flexible chain macromolecules in polymer solutions and melts are determined by their structure.[6,7] Indeed a flexible chain macromolecule consists of a large number of segments N capable of being oriented independently of one another and of executing definite types of motion. Thus, in constructing a molecular picture of the motion of chain molecules, it is essential to take into account the "duality" of the thermal motion. The displacement of a flexible chain macromolecule takes place as a result of the displacement of its elements (kinetic segments). The set of such displacements of the chain sections leads to the displacement of the centre of gravity of the entire macromolecule. The mobility of the chain segments is determined in its turn by the mobility of the elements of the system (their interaction): the segments of other chains (for a melt) or solvent molecules and chain segments (for a solution).

For the simplest chain model, where the motion of the chain is regarded as the motion of N non-interacting chain segments with a coefficient of friction of the segments ζ, the following expression has been obtained † for the self-diffusion coefficients D_R (motion of the Rouse type):[8]

$$D_R = kT/N\zeta, \quad (1)$$

where k is the Boltzmann constant and T the temperature.

It was postulated previously (and is still postulated in certain studies) that the coefficient of friction of the segments ζ is proportional to the macroscopic viscosity of the medium η. This is true only for low-molecular-weight substances and dilute polymer solutions.

Analysis of numerous experimental data[11] for low-molecular-weight liquids has shown that the following relation holds for them:

$$D\eta = \frac{N_A kT}{4\sqrt{2}} \left(\frac{\rho}{MN_A}\right)^{1/3},$$

where ρ is the density of the liquid and N_A the Avogadro number. The dependence of $D\eta$ on $M^{-1/3}$ is characteristic of molecular models in the form of a sphere moving in a medium having a viscosity η.

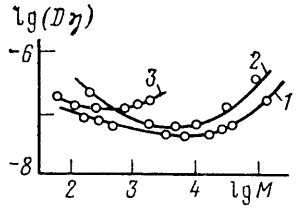


Figure 1. Dependence of $\lg(D_\eta)$ on $\lg M$ for polydimethylsiloxane (curve *1*), poly(ethylene oxide) (curve *2*), and polyethylene (curve *3*) according to the results of Budtov and Konsetov[16] and Tanner et al.[29]

However, with increase in the polymer concentration and in the molecular weight (M) of the chain (for solutions and for the melt), the quantity ζ is no longer determined by the macroscopic viscosity η. Fig. 1 illustrates the dependence of $D\eta$ on M for certain polymers.[12–14] Evidently, $D\eta$ varies with increasing M in a complex manner, although it follows from the simplest relation (1) that it should only decrease with increase in M (or N). Thus the classical ideas of the hydrodynamics of a continuous medium are inapplicable in the interpretation of the diffusion phenomena in flexible chain macromolecules.‡

† An analogous model has been proposed by Kargin and Slonimskii independently of Rouse.[9,10] The viscoelastic properties of polymeric materials have been calculated on the basis of this model.

‡ This apparently evident assertion was nevertheless not recognised for a long time, which led to a significant retardation of the development of ideas about the diffusional mobility of macromolecules.

We shall consider the displacement of an element X of a diffusing macromolecule.[15,16] Suppose that the medium surrounding the polymer chain consists of low-molecular-weight substances (a low-molecular-weight solvent) (Fig. 2*a*). Having received momentum from a certain section of the selected chain, the solvent molecule can move away from the initial position sufficiently "far" and "fast". The mean square of the displacement of the solvent molecule is $\langle X_S^2 \rangle = 2D_S t$, where D_S is the diffusion coefficient of the solvent molecule and t is the time. Nothing inhibits its motion apart from the natural viscous retardation determined by the viscosity of the solvent η_S.

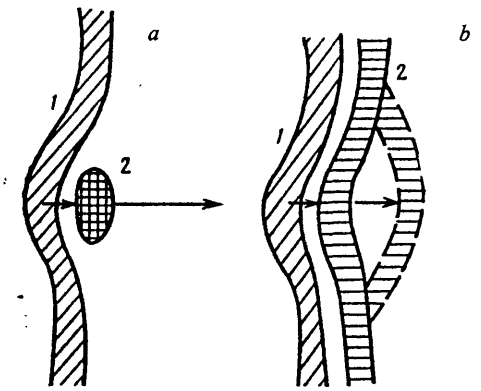


Figure 2. Schematic representation of the molecular picture of the motion of a chain molecule in a low-molecular-weight solvent (*a*) and in the melt (*b*).

Another situation arises if the medium consists of long flexible chain macromolecules (melts) (Fig. 2*b*). When a unit of a selected molecule is displaced, an elementary unit of the chain molecule surrounding the specified molecule is also displaced. However, this elementary unit cannot move away from the initial position sufficiently "far" and "fast", since it is bound to the macromolecule "at rest". The rate of displacement of this section is determined not only by its local characteristics (the size of the segment and the local viscosity of the medium) but also by its elastic linkage with the entire macromolecule and by its overall displacement. Fig. 3 presents the time variation of $\langle X_A^2 \rangle$ of an elementary unit of a chain macromolecule for the simplest Kargin–Slonimskii–Rouse model. It is seen that the longer the time of the observation, the smaller the contribution of the displacement of the element of the polymer chain compared with the displacement of the solvent molecule $\langle X_S^2 \rangle$. Fig. 3 illustrates this in a generalised form: $\langle X_A^2 \rangle / \langle X_S^2 \rangle = f(t/t_A)$.

Thus we cannot speak of the "constraint" of the transverse motion of a chain macromolecule, or about the anisotropy of the diffusional motion of a chain, or about topological limitations of the diffusional mobility, for which an attempt has been made to describe them in terms of the so called "quasi-network".

A molecular model for the diffusional motion in such systems has been proposed by de Gennes[17,18] (see also Gotlib et al.[6]). It has been shown that the square of the displacement of the elementary unit is

specified by the relation

$$\langle X_A^2 \rangle = 2A\sqrt{D_A t/\pi}, \quad t_A < t < \tau, \tag{2}$$

where D_A is the diffusion coefficient of the segment, $t_A = A^2/2DA$, τ is the relaxation time of the entire chain, and A is the size of the segment.

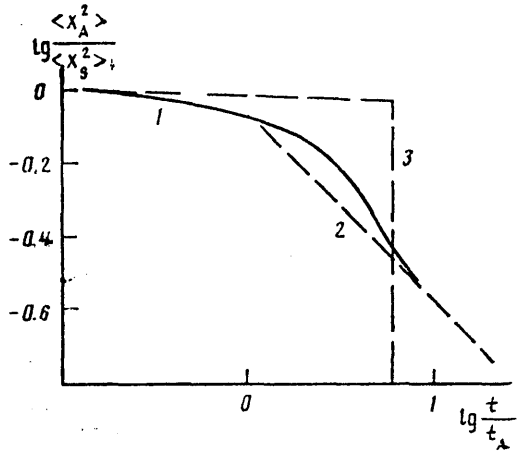


Figure 3. Dependence of $\lg(\langle X_A^2\rangle/\langle X_S^2\rangle)$ on $\lg(t/t_A)$ calculated for the Kargin–Slonimskii–Rouse model (curve *1*) and for the reptation model (curve *2*) [Eqn. (2)]; curve *3* represents the corresponding dependence of the transverse displacement for the "tube" model.

Thus a radical alteration of the mobility of the elements of the medium is characteristic of concentrated polymer solutions and melts. The displacement of the specified macromolecule by changing places with solvent molecules, observed previously for dilute solutions in a low-molecular-weight solvent, is no longer attainable for melts. The diffusional motion in a viscoelastic medium takes place in two ways. On the one hand, this is a specific motion of a section of a specified macromolecule, which involves only "local" changes in the conformation of the surrounding medium. On the other hand, this is the motion of the segment over long distances (owing to topological limitations, such motion occurs in only one direction) along the chain. The terminal chain element moves "ahead" and drags behind it the entire chain, i.e. a "snake-like" type of motion is observed—the reptation type of motion. The molecular theory of this type of motion, applied to the calculation of the viscoelastic properties of polymeric materials, has been developed in a number of studies.[17–19] In later studies, it has been used widely to develop a molecular theory of liquid-phase polymers.[6]

We shall consider below in greater detail the application of reptation motion to the description of the diffusion of chain molecules. Here one would wish to note that the reptation type of motion can be readily modelled by considering the motion of the chain in a "tube", whose configuration resembles the configuration of a flexible chain macromolecule[20,21] (Fig. 4).

Indeed in Fig. 3 we can replace the smooth decrease in $\langle X_A^2\rangle$ with increase in t by a stepwise decrease (curve *3*). This means that, for long times, one no longer observes a transverse displacement of the segment ($\langle X_A^2\rangle = 0$), i.e. an "impermeable" wall is thereby introduced. This limit in fact determines the "tube" diameter. It amounts to several segments (t/t_A at the boundary is ~ 5).

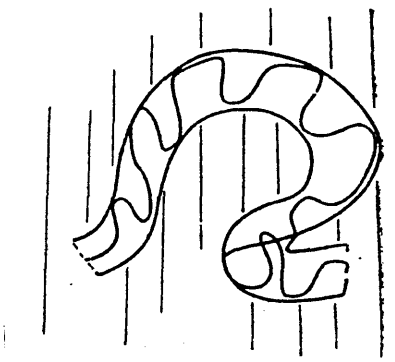


Figure 4. The "tube" model for the study of the reptation motion of the chain.

In order to characterise the configuration of the "tube", the parameter b, which is an analogue of the persistent length of a chain macromolecule, has been introduced.[22] The mean square of the distance between the ends of the "tube" is then given by

$$B^2 = Lb - \frac{b^2}{2}[1 - \exp(-2L/b)], \tag{3}$$

where L is the contour length of the "tube", i.e. the length of the fully straightened "tube". The quantity b characterises the degree of twist of the configuration of the "tube": the smaller the value of b, the more twisted is the "tube". For $L < b$, we have $B^2 = L^2$, i.e. the "tube" has the configuration of a rod, while for $L > b$, we obtain $B^2 = Lb$,[17–19]§ whereupon $b > A$. Whereas the size of the chain segment A is determined by the chemical structure of the chain, the quantity b depends on the structure of the molecules of the medium surrounding the specified macromolecule. For example, b may depend on the deformation, degree of cross-linking, and concentration of the polymer in the matrix through which the labelled macromolecule diffuses.

The introduction of the concept of curvature of the tube (or curvature of the reptation path of the diffusing macromolecule) is of fundamental importance, since it permits a molecular interpretation of concepts widely used in the physical chemistry of polymers such as the critical molecular weights M_c. For $M < M_c$ (or $L < b$), the chain behaves as a Rouse chain, whereas for $M > M_c$ (or $L > b$), the twisting of the chain and the topological limitations of the mobility of the macromolecule are fully manifested.

An attempt is usually made to interpret M_c as the distance between the nodes of a "quasi-network". For solutions, such a representation is possible. However, it is clearly inapplicable to melts, since in a melt it is impossible to specify the characteristic

§ The case $L \gg b$ was also considered in the above studies.[17–19]

point of the interaction between the specified chain and other chains, since this interaction is uniformly distributed along the chain. If a "node" with a definite lifetime τ_c is introduced into the model for the melt as a characteristic of the interaction,[22] then naturally the number of nodes N_c, hindering diffusion, will depend on the velocity of the motion v:

$$N_c = \frac{N_c(0)}{\exp(A/v\tau_c) - 1}.$$

Hence it follows that the translational friction coefficient $\Lambda = \Lambda_0(1 - N_c)$, where $N_c(0) = N_c(v \to 0)$ and $\Lambda_0 = \Lambda(v \to 0)$. Estimates have shown[22] that, for self-diffusion processes, the quantity $A/v\tau_c$ ranges from 10 to 10^6 and the influence of the nodes arising in the system can be disregarded.

We shall consider below the application of the above ideas to the analysis of experimental results obtained in recent years.

III. Self-diffusion coefficients of chain macromolecules in the melt

1. General relations

The dependence of the self-diffusion coefficient D on the molecular weight M has been investigated for a fairly large number of flexible chain polymers (PE, PDMS, PEO, PI, BSR)¶ (Fig. 5). These data have been analysed.[16] The data published subsequently[23–27] confirmed the earlier relations. The dependence of D on M can be described empirically by the relation

$$D = KM^{-\alpha}, \qquad (4)$$

where the numerical coefficient α is in the range from +1.3 to +2.0 and K is an empirical constant. These relations were confirmed in subsequent studies and the upper limit of α reached 2–2.4.[3–5]

However, the most interesting data were obtained when self-diffusion processes were investigated with variation of the molecular weight M_m of the surrounding medium.[28–30] The dependence of D on the molecular weight of the diffusing macromolecule (M) and on the length of the macromolecule in the surrounding medium (P) makes it possible to elucidate the characteristic features of the diffusional behaviour in such complex systems.

Fig. 6 illustrates the dependence of P for "labelled" PS macromolecules in a matrix comprising PS macromolecules on the molecular weight M_m of the matrix as far as weakly cross-linked gels ($M_m = \infty$).[28] Evidently, with increase in the molecular weight of the diffusing chain (M) and of the matrix (M_m), D diminishes. However, for sufficiently large values of M_m (up to weakly cross-linked gels—see also Zakharov[31]), the quantity D no longer depends on M_m. Similar data have been obtained also for PDMS,[29] PS,[30] and polyisoprenes.[31] An interesting result of Zakharov's study has been the establishment of the fact that the variation of D as a function of M depends on the method of preparation of the matrix (the method used for its deformation and annealing). The dependence of D on the deformation of the medium is clearly manifested: with increase in deformation, D fell.[31,32] However, for non-annealed elastomers, the coefficient D could actually increase on extension of the material.

¶ The following notation has been adopted: PE = polyethylene, PDMS = polydimethylsiloxane, PEO = poly(ethylene oxide), PI = polyisoprene, and BSR = butadiene–styrene rubber.

The dependence of D on M and M_m makes it possible to determine not only the values of α but also the differential indices α_N and α_P, i.e.

$$\alpha_N = d\lg D/d\lg M;$$
$$\alpha_P = d\lg D/d\lg M_m,$$

which will be analysed below.

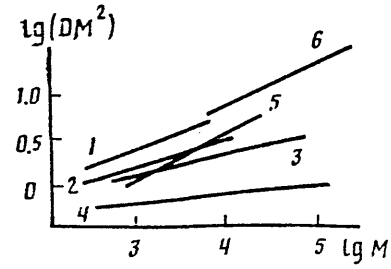


Figure 5. Dependence of $\lg(DM^2)$ on $\lg M$ for melts of certain polymers:[16] *1*, PE; *2* and *3*, PDMS; *4*, PEO; *5*, PI; *6*, BSR.

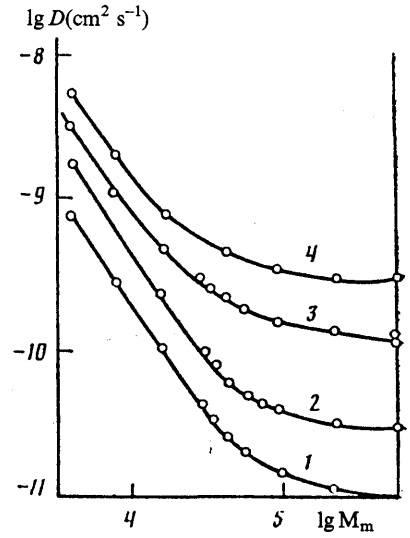


Figure 6. Dependence of $\lg D$ for a trial chain on $\lg M_m$ of the surrounding medium for PS molecules in a polystyrene matrix (T = 212 °C); 10^{-4} M: *1*, 10; *2*, 5.8; *3*, 3.0; *4*, 1.8. The points on the right-hand axis represent diffusion in a weakly cross-linked gel.

2. The motion of a chain through a weakly cross-linked gel

We shall consider the motion of a chain through a matrix with infinitely large molecules, i.e. a weakly cross-linked gel.[20] Suppose that the "local" molecular motion has developed fairly strongly and is characterised by a segment diffusion coefficient D_A. This is the

most direct instance of the manifestation of the reptation motion of a macromolecule: the chain can move only via the terminal element. Suppose that the length of the macromolecule is L ($L = NA$). Using the distance between the nodes of the quasi-network (N_c is the number of segments between quasi-cross-links), one can write the following formula for the overall length of the axial line of the tube:[17]

$$L_\tau = NA/N_c^{0.5} = L/N_c^{0.5}.$$

It follows from Eqn. (1) that the diffusion coefficient of the macromolecule within the tube is $D_T = D_A/N$. The time τ required for the chain to leave the initial tube is given by

$$\tau = \frac{l_\tau^2}{2D_\tau} = \tau_A \frac{N^3}{2N_c}, \quad (5)$$

where τ_A is the relaxation time of the segment. Although the chain migrates along the tube over a distance L during the time τ, nevertheless in space this migration is much smaller, since the tube is strongly bent [see Eqn. (3)]. The mean square of the displacement of the chain† during the time τ is $<X^2> = LA$. The following relation can then be obtained for the self-diffusion coefficient:[20]

$$D_{DG} = \frac{LA}{2\tau} = \frac{D_A N_c}{N^2} = D_R \frac{N_c}{N}. \quad (6)$$

Thus, for a very long chain, we have $D \propto N^{-2}$ in contrast to $D \propto N^{-1}$ for a short chain [see Eqn. (1)], i.e. Eqns. (1) and (6) yield the limiting laws governing the dependence of D on N.

Real macromolecules have a finite molecular weight. Calculations of the dependence of D on N for chains with a finite molecular weight have been performed.[22] The mean square of the displacement of the terminal chain element B^2 along the tube is specified by Eqn. (3). Since the relaxation time of the chain in this tube is $\alpha_T = L^2/2D_T$, we obtain finally

$$D_B = \frac{B^2 D_A}{L^2 N} = \frac{D_A}{N}\frac{B^2}{L^2}. \quad (7)$$

When $L < b$, we have $B^2 = L^2$ [see Eqn. (3)] and $D_B \propto D_A N$, i.e. the Rouse formula is obtained, whereas in the case where $L > b$ we obtain $B^2 = Lb$ and $D_B \propto D_A b/NL$, which corresponds to the de Gennes formula if it is assumed that $b = N_c A$. In the general case $D \propto N^{-1}$—N^{-2} [between N^{-1} and N^{-2}] and α is in the range from 1 to 2 [see Eqn. (4)].

We shall compare quantitatively the theoretical and experimental data. Here, we shall consider only the results of the study of the diffusion coefficients of a "trial" macromolecule diffusing in a matrix with an infinite molecular weight. We shall designate this value of D by D_∞. It is convenient to analyse the values of $D_\infty M$, whereupon Eqn. (7) is transformed into

$$D_\infty M = D_A M_A (B^2/L^2). \quad (8)$$

Fig. 7 illustrates the dependence of $\lg(D_\infty M)$ on $\lg M$ for PDMS [29] and PS [28,30] melts and also the dependence of $\lg(B^2/L^2)$ on $\lg(L/b)$ calculated by Eqn. (3). Evidently the theoretical curves reproduce correctly all the characteristic features of the experimental curves. A quantitative agreement can be obtained if the following values are selected: $D_A M_A = 4 \times 10^{-4}$ cm^2 s^{-1} and $M_b = 5 \times 10^3$ for PDMS and $D_A M_A = 6.3 \times 10^{-6}$ cm^2 s^{-1} and $M_b = 1.2 \times 10^4$ (D = 212 °C) for PS, M_b being the molecular weight of a chain section with a length b. The quantities M_b are close to the "critical" molecular weights obtained from rheological data. The quantities $D_A \simeq 10^{-6}$ cm^2 s^{-1} (PDMS) and $D_A \simeq 10^{-8}$ cm^2 s^{-1} (PS) have reasonable values. For example, for M = 746, the experimental D is 2.2 × 10^{-6} cm^2 s^{-1}. The data obtained permit the claim that a quantitative agreement is observed between the theoretical and experimental results for melts with $M_m = \infty$.

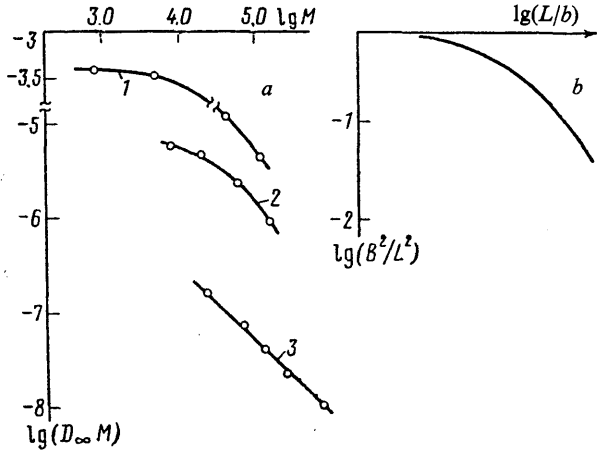


Figure 7. Dependence of $\lg(D_\infty M)$ on $\lg M$ (*a*) and of $\lg(B^2/L^2)$ on $\lg(L/b)$ (*b*) [the curve was calculated by Eqn. (3)]: *1*, PDMS;[29] *2* and *3*, PS.[28,30]

It is seen from the above analysis that, when $M < 10^3$ (PDMS) or $M < 10^4$ (PS), the diffusional motion of the macromolecule is of the Rouse type ($D \propto M^{-1}$). Only when $M > 10^4$ (PDMS) and $M > 10^5$ (PS) can one claim that the reptation type of motion is fully achieved. This means that, when $M > 10M_b$, the topological limitations by the surrounding medium on the mobility of the macromolecular chain are decisive. In view of such "diffuse" transition from one type of motion to another (a $10M_b$ range), the different literature values of "critical" molecular weights determined by different methods become understandable. Here it is essential to note that the study of the self-diffusion of "labelled" macromolecules provides a unique possibility for varying separately both the molecular weight of the diffusing chain and the molecular weight of the surrounding medium. In the usual rheological studies these two parameters are varied simultaneously, which hinders a quantitative interpretation (see the next Section).

3. Motion through a matrix with a finite molecular weight

Together with the diffusion of a chain along the tube, the process involving the renewal (relaxation) of the tube itself, as a result of the motion of other chains constituting the tube, take place.[17] The self-diffusion coefficient of the macromolecule in the melt (D_1) is then given by

$$D_1 = D_R + D_P, \quad (9)$$

where D_P is the component of D associated with the relaxation of

† The mean square of the distance between the ends of a chain with a length L is $NA^2 = LA$.

the tube and D_B is specified by Eqn. (7). The existing model theories have shown that D_P is proportional to N_c/P, N_c^2/P^2, and $N^{0.5}(N_c^2/P^3)$ [20,33,34] (here P is the number of segments in the matrix macromolecule surrounding the trial chain with a length N). Unfortunately the question of the selection of a particular dependence is so complex that fairly arbitrary hypotheses concerning the nature of the phenomenon are put forward in the studies mentioned above. One cannot therefore give preference at the present time to any one model and we therefore used the approach of the scaling theory for the description of the dependence of D_P on N.[35,36] We adopt the following functional relation for D_P (when $P > N_c$):

$$D_P = \frac{D_A}{N}(\gamma N_c/P)^n Z, \qquad (10)$$

where γ and n are empirical coefficients and Z is the probability that the molecule is located in the tube, i.e. is subjected to topological limitations by the surrounding medium as regards motion across the contour line:

$$Z = 1 - \exp[-(P - N_c)/N_c].$$

When $P < N_c$, we have $Z = 0$ and, when $P > N_c$, we have $Z = 1$.

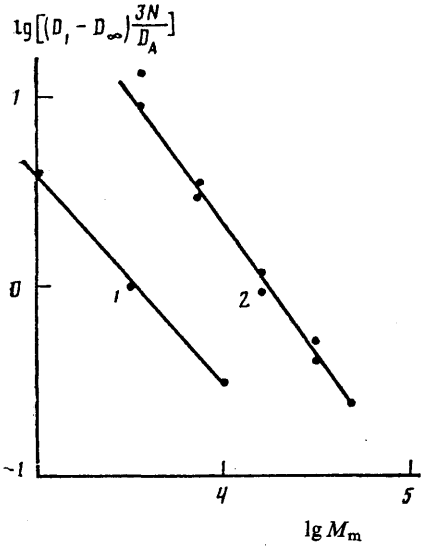


Figure 8. Dependence of $\lg[(D_1 - D_\infty)(3N/D_A)]$ on $\lg M_m$ for PDMS (curve *1*) and PS (curve *2*) according to different data.[28-30]

The coefficients γ and n can be found by analysing the experimental data. Suppose that $P > N_c$ ($Z = 1$). We then examine the variation of $(D_1 - D_\infty)(3N/D_A)$ as a function of M_m. Fig. 8 illustrates the dependence of $\lg[(D_1 - D_\infty)(3N/D_A)]$ on $\lg M_m$ for PDMS [29] and PS.[28] The quantities n (1.1 for PDMS and 1.4 for PS) and γ (0.28 for PDMS and 0.12 for PS) can be determined from the straight lines presented. The similarity of the empirical coefficients n and γ obtained for different objects shows that the hypotheses put forward are reasonable.

Thus we obtain finally for the self-diffusion coefficients of the melt[35,36]

$$D_1 = \frac{D_A}{N}\left[\frac{Lb - \frac{b^2}{2}[1 - \exp(-2L/b)]}{L^2} + Z\left(\gamma\frac{N_c}{P}\right)^n\right]. \qquad (11)$$

Fig. 9 presents the theoretical dependences of D_1M/D_AM_A on M_m/M_b for different values of M and n. Evidently the self-diffusion coefficients presented decrease with increase in M_m and tend to a limit which is independent of M_m (cf. Fig. 6). The observed relations are consistent with experimental data.

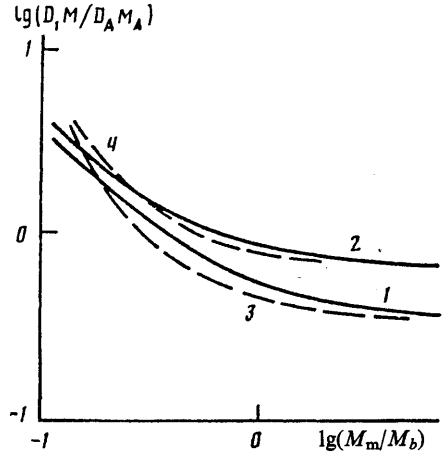


Figure 9. Dependence of $\lg(D_1M/D_AM_A)$ on $\lg(M_m/M_b)$ calculated by Eqn. (11) for $n = 1$ (curves *1* and *2*) and $n = 1.5$ (curves *3* and *4*) ($\gamma = 0.2$) with $N/N_c = 2.5$ (curves *1* and *3*) and $N/N_c = 0.5$ (curves *2* and *4*).

In the study of the dependence of D on M, the molecular weights of both the moving chain and of the surrounding medium are usually varied, i.e. $N = P$. Fig. 10 illustrates the dependence of D_1M/D_AM_A on M/M_b for $N = P$ calculated by Eqn. (11). In the range where $N > N_c$, the contribution of the second term in brackets is insignificant, i.e. the role of the "tube" renewal processes is the self-diffusion phenomenon is insignificant in this range of N. For $N \simeq N_c$, the "tube" renewal process can already play a definite role and when $N < N_c$ the very concept of the "tube" and reptation loses physical significance. Thus the second term in Eqn. (11) is significant only in the region where $N \simeq N_c$. Fig. 10 also illustrates the $D \propto N^{-2}$ relation, which gives rise to the $D(N)$ limiting law at $N \to \infty$. Evidently the straight line obtained in terms of logarithmic coordinates is close to the curve calculated from Eqn. (11). Allowance for the second term in Eqn. (11) then expands the region of applicability of the $D \propto N^{-2}$ law to cover also the region of low molecular weights. Fig. 10 also presents the dependence of D_∞ on M plotted in terms of the approximate formula

$$D_\infty = \frac{D_A}{N}\frac{1}{1 + L/b}. \qquad (12)$$

This relation is more convenient for analysis and actually agrees with the more accurate relation (7).

Thus it is seen that the relations obtained describe quantitatively the behaviour observed for self-diffusion coefficients in melts.

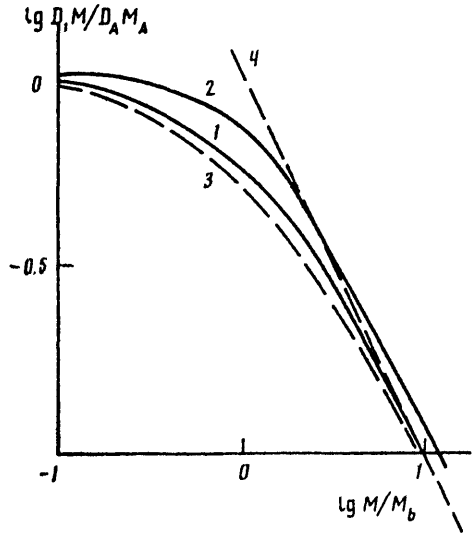


Figure 10. Dependence of $\lg(D_1M/D_AM_A)$ on $\lg(M/M_b)$ calculated by Eqns. (8) (curve *1*) and (11) (curve *2*) for $N = P$. Curve *3*, calculated from the approximate formula (12), and curve *4*, representing the limiting law governing the variation of D with M ($D \propto N^{-2}$), are presented for comparison.

IV. Self-diffusion in concentrated polymer solutions

1. General relations

In the region of dilute solutions, the theory of the translational mobility of macromolcules has been developed using Kirkwood's ideas about intermolecular hydrodynamic interactions between the elements of a chain macromolecule. The simplest relation for D when $c \to 0$ (D_0) is

$$D_0 = \frac{kT}{N\zeta}(1 + 1.843\sqrt{N}), \qquad (13)$$

where c is the concentration in g cm^{-3}. For more accurate and complex relations, see Rafikov et al.[7] All the available experimental data indicate a satisfactory agreement between the theoretical and experimental relations in the region of very dilute solutions.

The concentration dependence of D in the region of moderate concentrations has been investigated for certain systems in fair detail.[1,2] In the first studies, the authors concluded[37–39] that the scaling relations hold fairly well for the $D(c, M)$ function. It is essential to note tht the studies were performed in a restricted concentration and molecular weight range. However, in later investigations[40–45] a discrepancy between the predictions of the scaling theory and experimental relations was noted. The range of experimental concentrations of the solutions was greatly extended by Sundukov et al.[43] Fig. 11 [43] presents the dependence of D on c for solutions of poly(ethylene oxide) in dioxan.

Proceeding to the analysis of the dependence of D on c (or the volume concentration φ), it is necessary to take into account in the first place the variation of D_A (or ζ) as a function of φ. Failure to take into account the variation of the segmental mobility with increases in concentration has led in some of the early studies to incorrect conclusions. The variation of D_A (or ζ) with φ is usually described by a relation obtained on the basis of the free volume theory [see Eqn. (22) below]. The variation of D_A with φ can be taken into account more rigorously by an experimental procedure. The determination of the dependence of the self-diffusion coefficient of the solvent D_S on φ appears to be most correct.[16] In some investigations, it has been suggested that the spin–lattice relaxation times,[13,46] the monomeric friction coefficients determined from the viscoelastic properties of solutions,[44] etc. can be used to determine the dependence of D_S on φ. Below, we shall consider the reduced self-diffusion coefficient $\tilde{D} = D/D_A$. The quantity $\tilde{D}$ no longer depends on the variation of the local mobility with increasing concentration of the polymer solution.

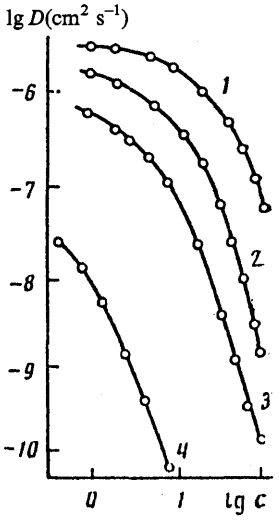


Figure 11. Dependence of $\lg D$ on $\lg c$ for PEO solutions in dioxane; 10^{-4} M: *1*, 0.2; *2*, 2; *3*, 4; *4*, 30.[43]

As in the analysis of the dependence of the viscosity of polymer solutions on concentration,[16] it has been suggested in some studies that generalised coordinates be employed for the representation of the dependence of D on c for solutions of different fractions. Thus the present author[15,47] proposed the generalised coordinates $\tilde{D} - c[\eta]$ (Fig. 12), while Sundukov et al.[43] proposed $D - (c/c_p)$, where c_p is an empirical quantity selected for each solution with a given molecular weight (Fig. 13).‡ In terms of these coordinates, it is possible to obtain a generalised dependence of D on c and M for solutions having different molecular weights in solvents of different kinds

‡ Here it is essential to note that the dependence of c_p on M is close to that of $[\eta]$ on M.

(differing in the interaction between the solvent and polymer molecules) and for polymers with different chemical structure of the chain.[47]

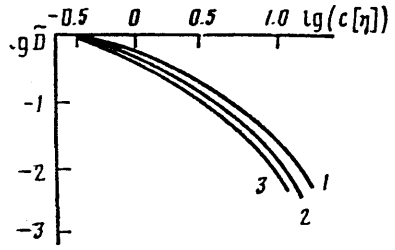


Figure 12. Dependence of $\lg \tilde{D}$ on $\lg\{c[\eta]\}$ for PS (curve *1*), PDMS (curve *2*), and PEO (curve *3*) solutions.

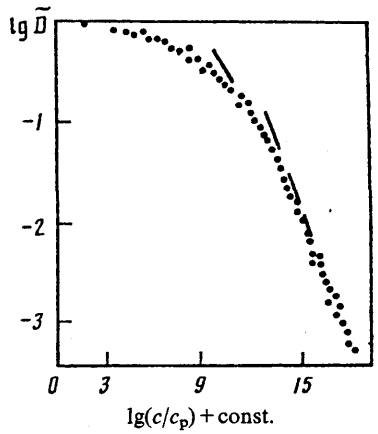


Figure 13. Dependence of $\lg \tilde{D}$ on $\lg(c/c_p)$ for PEO solutions in dioxane.[43] Data for different fractions are presented (see the caption to Fig. 11).

2. Theoretical relations for D in concentrated solutions

The main experimental relations between D and M have been explained by the present author.[36,47] Indeed, in the analysis of data for moderately concentrated solutions it is necessary to take into account the presence of the units of other macromolecules whose interaction with the units of the main chain diminishes the intramolecular hydrodynamic interactions of the selected macromolecule. There is no rigorous solution of this type of problem. However, the use of the "effective hydrodynamic field" model for the description of the hydrodynamic interactions of elements moving in a viscous liquid[48,49] proved successful. An equation for the dependence of D on M and φ was obtained:[47]

$$D(\varphi) = \frac{kT}{N\zeta}[1 + 1.843\sqrt{N}\exp(-1.27\sqrt{c[\eta]})]. \qquad (14)$$

Eqn. (14) is valid in the following concentration ranges: $1 < c[\eta] < c^*[\eta]$, where $c^*[\eta] = 0.64(\ln 2\sqrt{N})^2$. For the usual values of N, the upper limit is $c^*[\eta] \simeq 10-15$.

Fig. 14 illustrates the dependence of $\lg \tilde{D}$ on $\sqrt{c[\eta]}$ for PS, PDMS, and PEO. In terms of these coordinates, linear $D = f\{c[\eta]\}$ relations are observed and can be described by the following empirical equation:

$$\ln(\tilde{D}/\tilde{D}_0) = -(1.15-1.4)\sqrt{c[\eta]}. \qquad (15)$$

The slopes of these relations (1.15 – 1.4) are close to 1.27 [see Eqn. (14)].

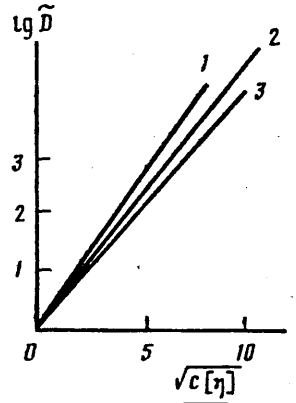


Figure 14. Dependence of $\lg D$ on $\sqrt{c[\eta]}$ for solutions of different polymers: *1*, PDMS; *2*, PS; *3*, PEO.

The values of α in Eqn. (4) vary continuously with c from +0.5 to 1 in contrast to the stepwise variation, predicted by the scaling theory, from $1(c < c^*)$ to $2(c > c^*)$. The dependence of α on $c[\eta]$ then differs somewhat for different values of N (Fig. 15*a*).

The influence of the molecular weights of the moving macromolecule and of the surrounding medium on the $D(c)$ relation have been considered separately.[35] In conformity with the notation adopted for the specified macromolecule and the macromolecules of the surrounding medium (N, P), the following equation can be written for the $D = f(c)$ relation:

$$D = \frac{D_A}{N^{0.5}}\left[\frac{1}{1.843N^{0.5}} + \exp(-1.27\sqrt{c[\eta]})\right].$$

Here $[\eta] = 0.6\bar{v}P^{0.5}$, where $\bar{v}$ is the specific partial volume. In these equations, the exponents of N and P are 0.5 (θ-conditions).

3. Self-diffusion in concentrated polymer solutions

In this concentration range, there are in fact no experimental data for the dependence of D on c and M. However, the existence of experimental and theoretical data for moderate concentrations and for polymer melts makes it possible to obtain reasonable relations also for high concentrations. The scaling theory can be used conveniently to describe the dependence of $\tilde{D}$ on φ.[35,36,47] The dependence of $\tilde{D}$ on φ is usually considered in the form

$$\tilde{D} = \tilde{D}_R(\varphi/\varphi_{th})^{\beta}(\varphi > \varphi_{th}), \qquad (16)$$

where φ_{th} is the threshold concentration proportional to $[\eta]^{-1}$ and β is a numerical coefficient. β is found from the condition $D(\varphi \to 1) \propto N^{-2}$.

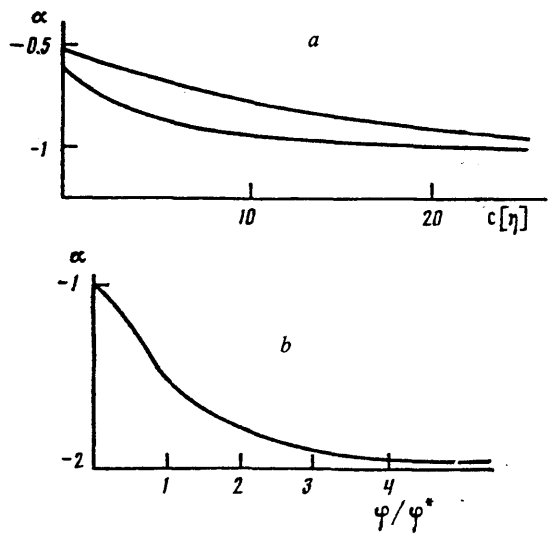


Figure 15. Dependence of α on $c[\eta]$ (*a*) and on φ/φ^* (*b*): *1*, $N = 10^3$; *2*, $N = 10^2$.

The scaling theory was first used to describe the $D(\varphi, M)$ function by Daoud and Jannink.[50] Since here we consider only the region of concentrated solutions (the θ-region), we have for the latter $\beta = -2$,[47] i.e.

$$\tilde{D} = \tilde{D}_R(1/\varphi^2 N). \tag{17}$$

However, the relations obtained in this way[47,50] suffer from one significant disadvantage. By analysing the $D \propto N^{-\alpha}$ relation [Eqns. (16) and (17)] we see that $\alpha = 1$ when $\varphi < \varphi_{th}$, $\alpha = 2$ when $\varphi > \varphi_{th}$ and α has no significance at the point φ_{th} when $\varphi = \varphi_{th}$. Naturally, there is in reality no such discontinuity in the dependence of α on φ.[37–45] This inaccuracy of the scaling theory has been removed[35] by invoking the concept of the reptation character of the motion of the macromolecule in the region of high concentrations.

We shall consider Eqn. (12). The quantity b (or N_c) is known to increase with decrease in concentration. Since the region of high concentrations is the region of the θ-solvent, it follows that, according to the scaling theory, we have

$$N_c(\varphi) = N_c/\varphi^2. \tag{18}$$

Substitution of Eqn. (18) in Eqn. (12) yields the following relation for the component D_∞ (when $\varphi > \varphi^*$):

$$D_\infty = \frac{D_A}{N}\,\frac{1}{1+\varphi^2 N/N_c}. \tag{19}$$

The quantity φ^* is determined from the equation

$$\varphi^* = \sqrt{N_c/N}. \tag{20}$$

For the usual polymers, $N_c \simeq 100$, whereupon $\varphi^* = 0.2-0.3$.

Evidently Eqn. (19) gives rise to a continuous transition from $D \propto N^{-1}$ to $D \propto N^{-2}$. Omitting the intervening stages, we quote the final relation:

$$\tilde{D} = \tilde{D}_R\left[\frac{1}{1+\varphi^2 N/N_c} + Z_\varphi\left(\gamma\frac{N_c}{\varphi^2 P}\right)^n\right], \tag{21}$$

where Z_φ is the probability that the macromolecule is in a tube at a specific concentration φ. For $\varphi < \sqrt{N_c/P}$, we then have $Z = 0$ [see also the explanation of Eqn. (10)]. The dependence of α on φ can be calculated from Eqn. (21) [see Eqn. (4)] (Fig. 15). Evidently, α varies continuously from 1 to 2. The $\alpha(\varphi)$ relation depends somewhat on the molecular weight of the surrounding medium.

The general dependence of D on φ (and not only the dependence of $\tilde{D}$ on φ) should take into account also the dependence of D_A (or D_S) on φ. The most generally accepted approach to the analysis of $D_S(\varphi)$ is associated with the "free volume" theory.[16] The simplest relation for the dependence of D_S on φ is

$$D_S = D_S(0)\exp\left\{-\frac{B_1\beta_1\varphi}{f_S(f_S-\beta_1\varphi)}\right\}, \tag{22}$$

where B_1, β_1, and f_S are parameters of the free volume theory.[12] For more complex relations governing $D_S(\varphi)$, see Budtov and Konsetov[16] and Budtov.[51] For a wide class of flexible chain polymers without specific interactions (hydrogen bonds, ionic bonds), the limits of the variation of the ratios B_1/f_S and β_1/f_S have been obtained: from 3 to 5 and from 0.25 to 0.4 respectively.[16] Interesting results concerning the influence of the size of the solvent molecules on these coefficients have been given.[52] For $d\lg D/d\lg\varphi$, we obtain

$$\frac{d\lg D}{d\lg\varphi} = \beta(\varphi) + \frac{B_1\beta_1^2\varphi}{f_S(f_S-\beta_1\varphi)^2}. \tag{23}$$

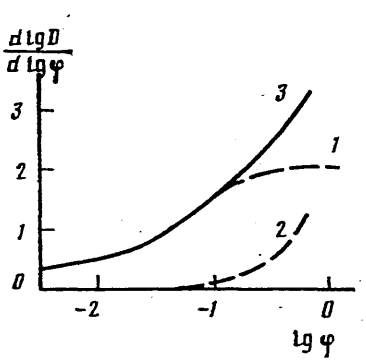


Figure 16. Dependence of $d\lg D/d\lg\varphi$ on $\lg\varphi$ calculated by Eqn. (23): *1*, the contribution of the first term in Eqn. (23); *2*, the contribution of the second term; *3*, the overall contribution.

Fig. 16 presents the dependence of $d\lg D/d\lg\varphi$ on the most typical representative of PS polymers (with toluene as the solvent). Evidently, when $\varphi \simeq 0.1$, the second term in Eqn. (23) constitutes an insignificant proportion of the first, while under conditions where $\varphi > 0.3$ it has to be taken into account.

Interesting studies have been initiated on self-diffusion processes during phase separation in polymer solutions.[53,54] Special methodological procedures have been proposed, which make it possible to estimate the self-diffusion coefficients in different phases from the non-exponential decay of the spin echo in NMR.

V. Characteristic features of the self-diffusion in oligomer melts and solutions

The relations discussed above are valid for fairly long chain molecules. When the self-diffusion of oligomers is investigated, other unusual dependences of D on M are observed.[55]§ The dependence of D on M for oligomers can be conveniently analysed in terms of the coordinates $(D_1/L_0)L - L$ (Fig. 17).¶ Evidently, in terms of these coordinates, D_1/D_0 for ethers and esters and also for n-alkanes initially diminishes with increase in L, but, when $L \simeq 30$ Å, the quantity D_1/D_0 no longer depends on L. If the end groups or other specific groups in the chain are in groups of atoms characterised by a strong interaction with the surrounding molecules, then the dependence of D_1/D_0 on L is different: the quantity increases with increase in L and subsequently attains a plateau. When the influence of the inhomogeneity of the chain structure can be disregarded ($L > 30$ Å), the ratio D_1/D_0 assumes the same value for all the systems investigated.

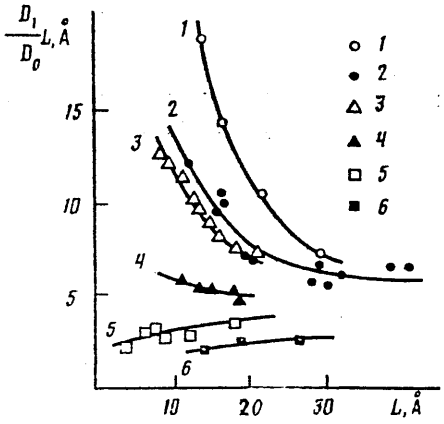


Figure 17. Dependence of $(D_1/D_0)L$ on L for different substances: *1*, ethers; *2*, esters; *3*, n-alkanes; *4*, phthalates; *5*, alcohols; *6*, acids.

The above effects can be accounted for using the free volume theory without resorting to the concept of aggregation. Indeed, it is well known that $f = f_0 + \Delta/N$, where f_0 is the fraction of the free volume for a homogeneous chain, N is the number of chain elements, and Δ is the increment in the ratio of the free volumes of the characteristic group and the repeating chain element. Then the diffusion coefficient of the oligomer D_{ol} depends on M in a complex manner:

$$D_{ol} = D_{hom}(M)\exp\left(\frac{\beta_L}{f_0}\frac{\Delta}{N}\right), \quad (24)$$

where D_{hom} is the diffusion coefficient for a homogeneous chain.

Indeed, in terms of the coordinates $\lg[(D_{hom}/D_0)L] - 1/L$, a set of curves, arranged fanwise, is observed and from their slopes it is possible to determine Δ for particular functional groups:

Group of atoms (or atom)	—O—	$-CH_3$	$-CH_2-$	C_6H_5-	>C=O	—OH	
Δ	5.4	1.7	0	—3.3	—3.5	—4.3	—11.5

The negative values of Δ indicate the retardation of the "local" motion of the corresponding group compared with the motion of the $-CH_2-$ group. These results make it necessary to treat with caution the interpretation of the dependence of D on M when low-molecular-weight polymers ($M < 10^4$) are considered. Unfortunately these effects are not taken into account in the majority of studies discussed.

VI. Numerical modelling of the translational mobility of macromolecules

The modelling of the mobility of macromolecules by means of direct computer simulation of molecular models by Monte Carlo (MC) and molecular dynamics (MD) methods has come to be widely used in recent years.[6] The first studies on the analysis of small scale movements of generalised polymer chains by the MD method were carried out Balabaev et al.[58] Subsequently this approach was widely employed for the solution of specific problems. However, the majority of calculations were limited to the consideration of lattice systems idealised to the maximum extent, while for a microscopic description of the system it is essential to take into account explicitly the interactions between all the species (atoms). This imposes significant limitations on the number of species and their dimensions (molecular weights) and also on the time of observation of the species.[59]

A significant achievement of the dynamic calculations in the study of condensed systems has been the demonstration of the fact that the widely held hypothesis that the diffusion of species in a simple monotonic liquid has a jump (activation) mechanism does not correspond to the real picture of molecular motion.[60] The molecular flux of species in such a liquid involve successive small displacements of the molecules. A negligibly small contribution of "large jumps" to the overall diffusional flux is observed. An appreciable influence by attraction forces on the relaxation of large chain fragments has also not been discovered.[61] This type of motion has in fact been taken into account by the "free volume" theory[16] [see Eqn. (22)].

It has been shown[62] that the mobility of the terminal chain elements differs from the mobility of the central elements, which is consistent with the observations made for oligomers (see Section V). The question of the anisotropy of the motion of the chain unit has been considered[63] for a liquid polymer. It was shown that for short observtion times, the tangential component of the mobility is smaller than the transverse component. However, for large observation

§ Similar effects have been observed also both for the viscosity η and for $[\eta]$ of oligomers.[56,57]

¶ Here D_1 and D_0 are the self-diffusion coefficients of oligomers for $\varphi = 1$ and $\varphi = 0$.

times, the units are able to diffuse over a distance close to the average distance between the nearest neighbouring macromolecules in the system. The surrounding chains hinder the motion of the chain considered and force the units to move preferentially along the chain contour, i.e. the anisotropy of the mobility is significant. For a dilute solution, the anisotropy of the mobility is manifested to the least extent. It is essential to note that attempts to observe reptation processes (the anisotropy of mobility) yielded a negative result in the studies of Baumgartner and Binder[64] and Evans and Edwards[65] due to the small chain length and the short observation time.[66]

Within the framework of the pseudostochastic Verdier–Stockmayer model, the dynamics of an assembly of particles has been investigated.[57,58] It was shown that $D \propto N^{-\alpha}$, increasing with increasing concentration (Fig. 15). The $<X^2> \simeq t^g$ relation also varies with increasing concentration: g diminishes to 0.2 (see above).

The diffusion of a chain macromolecule in a matrix with stationary elements which the diffusing chain cannot cross has been modelled on a computer.[69] The distance between such obstacles is d. It was found that[22] the dependence of $D(d)/D(\infty)$ on N^2/d is represented by a single curve regardless of the value of d. It coincides with the dependence of D on L/b specified by Eqn. (7) if it is assumed that $bA = 2d^2$. This relation ($bA = 2d^2$) resembles the familiar formula for the square of the length of a chain whose contour length is b.

Thus it is seen that the principal results of numerical modelling have been reflected in analytical models and have been observed experimentally. An important feature of computer modelling is that it is possible to obtain unique information about the local structure of the material.

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The experimental and theoretical results presented in this study show that the dependences of the self-diffusion coefficient on concentration and on the molecular weights of the diffusing macromolecule and of the surrounding medium have been fairly thoroughly investigated and can be described quantitatively. The influence of the interaction of the chain with the solvent on the self-diffusion coefficient has been discovered. The characteristic features of the diffusion of oligomers have been examined.

The relations obtained can be used to solve a wide range of problems in the physical chemistry of polymers.

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