Translated from *Uspekhi Khimii*, **55**, 679-709 (1986) U.D.C. 541.64:539.199

Computer Modelling of Dense Polymer Systems

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The application of the Monte Carlo method and the methods of molecular and Brownian dynamics to the study of the structures and dynamic properties of dense polymer systems with a strong intermolecular interaction is examined. The methodological problems arising in the computer modelling of polymers are discussed. Data obtained in numerical experiments on computers for solutions of macromolecules in a low-molecular-weight solvent, semidilute polymer solutions, liquid and amorphous polymers, as well as partly ordered systems (liquid and rotation crystals) are surveyed. The results of the computer experiments are compared with the conclusions arising from modern analytical theory. The limitations of the numerical methods and the prospects for their further development are considered.
The bibliography includes 195 references.

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I. INTRODUCTION

In connection with the progress in computer technology, methods involving the computer simulation of the mathematical models of various physical systems have come to be widely used in recent years. Such models include primarily those of many non-ordered systems with a strong interaction between species: molecular liquids, liquid metals, dense gases and plasma, polymer solutions and melts, liquid crystals, etc.

Three principal computer simulations methods are used in the solution of a whole series of problems in the physics and chemistry of polymers: the Monte Carlo method (MC) and the methods of molecular dynamics (MD) and Brownian dynamics (BD). In the MC method the required properties are obtained by averaging over an *ensemble* of configurations of the system generated on a computer with the aid of a suitable algorithm. The most detailed information (both equilibrium and dynamic) is provided by the MD method, which consists of the numerical integration of the equations of motion formulated in classical mechanics for all the particles of the system under specified initial conditions. The BD method yields a more detailed picture; in this method the influence of the medium (solvent) is taken into account as the overall effect of the forces of viscous friction and random forces.

In the vast majority of studies on the computer modelling of polymers (starting with that of Wall et al.),[1] the influence of volume (long-range) interactions on the conformation of an isolated macromolecule has been investigated by the MC method. The real macromolecule is usually represented in such calculations by a broken line executing random movements on a regular lattice of a specified type (cubic, tetrahedral, etc.). The surrounding solvent is not then taken into account explicitly on the assumption that its role reduces wholly to an effective renormalisation of the interaction potentials of the units of the macromolecule. There exist reviews of early studies in this field.[2-4]

The increase of the power of computers made it possible to formulate computer experiments with more complex models. On the one hand, it became possible to specify in greater detail the models of macromolecules themselves, including the calculations of data concerning chemical structure, inhibiting potentials, etc. Studies have been made on the modelling of a whole series of synthetic polymers,[5-9] polypeptides,[10] polynucleotides,[11] and polysaccharides (for example amylose[12] and cellulose derivatives).[13] On the other hand, the MC and MD methods have come to be used in the study of condensed polymer systems with direct allowance for the influence of the molecules of the medium and of the interaction between molecules. Such investigations are analysed in this review.

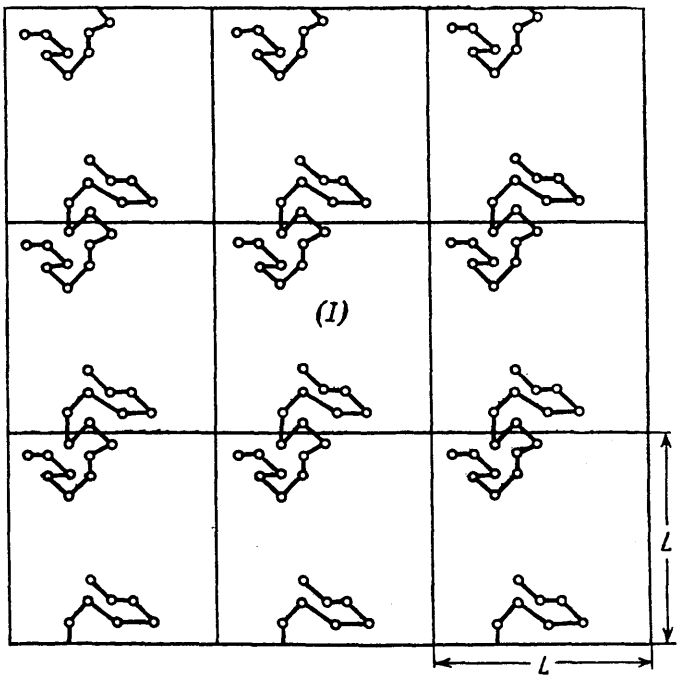


Figure 1. Planar projection of the computational cell (I) with periodic conditions on the boundaries. The cell contains one chain; the solvent particles are not shown.

II. DILUTE SOLUTIONS

1. Methodological Problems

In the computer modelling of dilute polymer solutions (macromolecule + dense low-molecular-weight liquid) all the particles (species) are placed in a cell which usually has the form of a cube with a specified edge L (Fig.1). In order to eliminate surface effects, periodic boundary conditions are introduced: the main cell is surrounded on all sides by similar cells. Free exchange of particles between the cells through the walls is possible. In addition, in dynamic methods a particle which enters the main cell from a neighbouring cell has the same momentum as the particle crossing the wall. We may note that the periodic conditions can be introduced in a different way by placing the molecules not in a cube but on the surface of a hypersphere with a specified radius and number of dimensions exceeding by unity that of the system being modelled.[14]

It is noteworthy that, among polymer systems, dilute solutions are the most inconvenient objects for computer modelling. The point is that, although the polymer molecule is of principal interest, nevertheless most computational effort is expended not on its investigation but on following the movement of solvent molecules, because the number of the latter in the cell is usually much greater than the number of polymer units. Indeed, in order to eliminate the interaction of the chains, it is necessary that the length of the edge of the cell should exceed the maximum size of the macromolecular chain. Consequently, in modelling even an extremely short chain, for example, one made up of 20 units with a contour having a length of ~20, the computational cell must contain ~10^4 solvent species when the density of the liquid, $\rho \cong 1$. Such systems lie at the limit of the capacity of the majority of modern computers. Furthermore, as in a physical experiment, the smallness of the observed effects is characteristic of the study of dilute solutions by computer methods. Before proceeding to the discussion of specific results, it is necessary to deal with certain new procedures for increasing the effectiveness of the calculations and also to examine the specific features which arise in the mathematical modelling of polymer systems.

We shall consider a system of N interacting particles with a specified pair potential $f(r_{ij})$, where $\mathbf{r} = (\mathbf{r}_1,\ldots,\mathbf{r}_N)$ are the radius-vectors of the particles which determine the configuration of the system and its potential energy:

$$U(\mathbf{r}) = \frac{1}{2}\sum_i^N \sum_j^N f(r_{ij}).$$

In the classical Metropolis scheme[15,16] the transitions between the configurations take place as follows. After a random selection of a particle i and its displacement in a random direction ($\mathbf{r}_i \to \mathbf{r}_i'$) over a distance $\leq\delta$, the transition to the new configuration ($\mathbf{r} \to \mathbf{r}'$) takes place with the probablilty

$$p = \min\{1,\ q(\mathbf{r},\mathbf{r}')\}, \qquad (1)$$

where $q(\mathbf{r},\mathbf{r}') = \exp[(U - U')/kT]$, U and U' being the corresponding potential energies. The system remains in the old state $\mathbf{r}$ with the probability $1 - p$. The formulation (1) means that p is equal to the smallest of the numbers in braces. The random selection process and the subsequent attempt to shift the particle (step) are repeated in the MC method a large number of times, s (~10^3–10^5 steps per particle); the required characteristic is averaged over all the s steps. The resulting estimate at $s \to \infty$ tends to the true mean over the canonical *ensemble*.

In order to accelerate the convergence of the computational procedure, it has been suggested[17,18] that the Metropolis scheme be modified in such a way that the selected particle moves with a higher probability in the direction of the instantaneous force acting on it from the sides of all the remaining particles. In this algorithm, called the "force bias method", the new configuration is achieved with a probability

$$p = \min\left\{1,\ q(\mathbf{r},\mathbf{r}')\cdot\frac{T(\mathbf{r}',\mathbf{r})}{T(\mathbf{r},\mathbf{r}')}\right\} \qquad (2)$$

where q is specified by Eqn.(1) and the quantity $T(\mathbf{r},\mathbf{r}')$, linked to the transition $\mathbf{r} \to \mathbf{r}'$, is determined from the formula

$$T(\mathbf{r},\mathbf{r}') = \begin{cases} C\cdot\exp(\lambda\Delta\mathbf{r}\cdot\mathbf{F}_i/kT) & \text{when } \Delta\mathbf{r} \leqslant \delta \\ 0 & \text{when } \Delta\mathbf{r} > \delta \end{cases} \qquad (3)$$

For the reverse transition, the quantity $T(\mathbf{r}',\mathbf{r})$ has an analogous form. In Eqn.(3), $\Delta\mathbf{r} = \mathbf{r}_i' - \mathbf{r}_i$ is the shift of the ith particle within the limits of the specified region δ, $\mathbf{F}_i = -\partial U(\mathbf{r})/\partial\mathbf{r}_i$ the force acting on the particle in the configuration $\mathbf{r}$, λ a parameter, and C the normalising constant, which cancels out in Eqn.(2). It is seen from Eqns. (2) and (3) that the particles are displaced predominantly in the direction of the force $\mathbf{F}$. For $\lambda = 0$, the scheme described reduces to the Metropolis scheme. The parameters λ and δ are chosen in such a way that the mean square shift of the particles is maximised.

A MC algorithm, formally similar to the method of Brownian dynamics, has been proposed[19–21] and Rossky et al.[19] called it SMART. If an N-unit chain is immersed in a viscous medium, then the movement of any ith particle (unit) can be described by the Langevin equation[22]

$$m_i\frac{d^2\mathbf{r}_i}{dt^2} = -m_i\gamma_i\frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i + \mathbf{R}_i, \quad i = 1, 2, \ldots, N, \qquad (4)$$

where m_i and γ_i are respectively the mass and the coefficient of friction, $\mathbf{F}_i$ is the force acting on the ith particle from the side of all the remaining particles of the chain, and $\mathbf{R}_i$ is a random force reflecting the random jolts by other molecules of the medium. In a real situation, Eqn.(4) should include the hydrodynamic forces, but one can consider a highly viscous medium ($\gamma \gg 1$) where they are absent. In this case the inertial term on the left-hand side of Eqn.(4) can also be rejected. The following algorithm of motion, formulated in the finite difference form

$$\mathbf{r}_i' = \mathbf{r}_i + \Delta t D_i\mathbf{F}_i/kT + \mathbf{X}_i, \quad i = 1, 2, \ldots, N, \qquad (5)$$

is then obtained. Here $|\mathbf{r}_i' - \mathbf{r}_i|$ is the distance traversed by the ith particle during the period Δt, $D_i = kT/m_i\gamma_i$ the diffusion coefficient of the particle, and $\mathbf{X}_i$ the random shift corresponding to the force $\mathbf{R}_i$ and having the normalised Gaussian distribution

$$W(X_{i\alpha}) = (4\pi a_i)^{-1/2}\cdot\exp(-X_{i\alpha}^2/4a_i), \quad \alpha = x, y, z, \qquad (6)$$

where $a_i = \Delta t D_i$ is the specified parameter.

In Brownian dynamics the equation of motion (5) describes a sequence of unconditional transitions between states. In the MC method the new position $\mathbf{r}'$ in Eqn.(5) is adopted or rejected with a probability defined by Eqn.(2), where

$$T(\mathbf{r},\mathbf{r}') = (4\pi a_i)^{-3/2}\cdot\exp\{-[(\mathbf{r}_i' - \mathbf{r}_i) - a_i\mathbf{F}_i/kT]^2/4a_i\}, \qquad (7)$$

and $T(\mathbf{r}',\mathbf{r})$ is formulated analogously. Compared with the standard scheme,[15] the "force bias" and SMART algorithms ensure an increase of the probability of the transition defined by Eqn.(1) by a factor of ~2–3.

Finally mention should be made of a fundamentally new approach to the MC modelling of chains based on the functional integration technique. In contrast to the usual treatment of the "chain–set of discrete force centres (units)" system, it has been suggested[23] that the macromolecule be described by a continuous line specified by a Fourier series in functional space. For a random selection of the series coefficients, the line changes its shape (i.e. it undergoes "conformational rearrangements") and the transitions between states evolve in accordance with the usual MC scheme.

In the study of polymers by the MD method, the problem of the way in which the valence bonds are described becomes important. Here there are alternatives: (1) the bonds can be modelled by any smooth function (for example, a quadratic function) and (2) the bonds can be regarded as absolutely rigid bounded formations, i.e. they are modelled by a δ-function. In the former case the standard difference schemes of computational mathematics are suitable for the integration of the equations of motion $m_i d^2\mathbf{r}_i/dt^2 = \mathbf{F}_i$,[24] which make it possible to find the coordinates and momenta of the particles at finite time intervals Δt. However, owing to the great "rigidity" of the valence potentials, high-frequency oscillations are characteristic of the chain particles which can be taken into account only for a very small integration step Δt. This shortens the length of the trajectory susceptible to calculations. For this reason, the exclusion from the calculation of the corresponding degrees of freedom when chemical bonds are treated as geometrical bounded regions gives rise to a considerable computational effect.

Within the framework of this method of modelling, special procedures, correcting the bond length at each step, are used. One of the correction procedures has been proposed by Balabaev[25] and another, the widely used procedure SHAKE, has been put forward by Ryckaert et al.[26] An improved version of the algorithm SHAKE, which the author called RATTLE, has been proposed.[27] The specific features of the mathematical modelling of polymers by the MD method consist precisely in the presence of such correction procedures. Without any changes, they also enter into the BD method, which is based on the numerical integration of the Langevin equation. The algorithms used at present for calculations by the BD method (including those taking into account hydrodynamic interactions[29] and the random force delay effects)[30] have been published.[28–30] Both dynamic methods yield a phase trajectory from which the equilibrium characteristics (as time averages) and the time variations are determined.

In conclusion of this Section, we shall make two general remarks: about the relation between the computer methods and about their correspondence to a real experiment. As already stated, the physical principles on which the MC and MD modelling is based differ radically. In the former case these are the probability principles of statistical mechanics and in the latter they are the extremely deterministic foundations of classical Newtonian mechanics. The BD method, in which stochastic and determined descriptions are combined, occupies an intermediate position in this sense.

The question of the equivalence of the equilibrium properties obtained by averaging with respect to the *ensemble* and time along the dynamic trajectory is actually identical with the familiar ergodic problem. If there exists a thermodynamic limit $(N, V)_{N, V \to \infty} = \text{const}$. (where V is the volume), then there is no doubt about the validity of the different types of averaging. Systems made up of a finite number N of particles require a more careful analysis. We may note that such a problem can be solved within the framework of the computer calculations themselves. It is found that the results of the averaging by both methods differ by a quantity of the order of $1/N$.

Another part of the problem of the relation between the computer methods reduces to the dynamic interpretation of the Monte Carlo process. This treatment is based on the fact that the Metropolis scheme (or its modifications) reproduces the evolution process in which the system passes step by step from one state to another and the consecutive states are highly correlated. Naturally, such evolution self-models a kind of artificial (stochastic) kinetics, but it does not reflect the real alternation of the states of the system in real time, as happens in molecular dynamics. Nevertheless, it is possible to define conditions for which the MC method yields the correct description of the kinetic behaviour. It has been recently demonstrated rigorously[31] that, within the limits of a small step ($\delta \to 0$), in the usual MC calculation the configuration relaxation is described by the same kinetic relations as in the modelling by the BD method at the limit corresponding to a high friction, where $\gamma \gg 1$ and the non-inertial movement of the particles follows the Langevin equation (5). The Monte Carlo time scale (i.e. the number of steps per particle) and the real time t are then linearly related: $s/N \cong Tt/\gamma\delta^2$, which is valid in practice for a fairly large step δ. Therefore, having followed by the two methods the evolution of any one function of the coordinates, it is possible to correlate the time scales and thereby establish a relation between the results of the statistical and dynamic modelling.

Thus the computer simulation methods, based on different physical principles, have a most important advantage—they are closed, i.e. there is a possibility of a mutual test within the very results obtained for the same model.

The principal problems in the computer experiment arise in connection with the formulation of the model of the test object. This concept includes primarily the set of rules describing the interaction of the particles with one another or with external fields. The way in which the valence forces, i.e. the chemical combination of atoms, are taken into account is one of the examples of such rules. Since different kinds of valence and non-valence potentials, which constitute merely an approximation to the true interaction, are used for this purpose, this in fact defines a measure of the correspondence between the physical and computer experiments. Naturally, initially it is possible to solve the converse problem, where the potentials are at first calibrated against the available experimental data and are only then used to obtain more detailed information about the system. On the other hand, since numerical experiments for the specified model yield rigorous results within the limits of statistical error, they can be adopted as a standard to test the theories relevant to an analogous model and the approximations on which the analytical treatment is based. We believe that this precise formulation of the problem is methodologically justified. However, in both cases one must remember (and this is the principal limitation) that any modern computer can operate only with an immeasurably smaller number of particles than in real systems, where $N \cong 10^{23}$. The "record" calculations, familiar to the authors, on the most powerful multiprocessor or vector computers (of the PS-3000 or CRAY type) are restricted to models comprising $N \cong 10^6$ particles and times $t \sim 10^{-6}$ s†, which are very small on the macroscopic scale. As a rule, calculations are in fact performed for $N \cong 10^2$–10^3 and a time interval $T \lesssim 10^{-9}$ s.

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†The symbol ~ is used in Russian to imply "proportional to", "of the order of", or even "approximately equal". No attempt has been made in the translation to elucidate its specific meaning in each use (Ed. of Translation).

Although small systems, such as molecular clusters or isolated macromolecules, are of independent interest, in the usual practice employed in computer calculations the interpretation of macroscopic properties on the basis of the modelling of a set of a small number of particles is an extremely non-trivial problem. The greatest difficulties are associated with the study of systems near phase transition points where large-scale low-frequency fluctuations arise. An extensive literature[16,24] has been devoted to the analysis of such problems, which we are unable to consider in detail here. We shall only note that, when periodic boundary conditions are used for the extrapolation to the thermodynamic limit, it is essential that the linear size of the cell $L(L \sim N^{1/d}$ in a d-dimensional space) should exceed significantly the correlation radius of the density fluctuations. If the calculation is not performed near a phase transition point, then for the usual short-range potentials this requirement is normally satisfied for $N \sim 10^2-10^3$ and the error due to the finite size is of the order of $1/N \sim 1/L^d$.

2. Equilibrium Properties

Since macromolecular compounds cannot be transferred to the gas phase, the question of the influence of the solvent on their conformation and movement is fundamental. It is important also from the methodological point of view. In fact the justification of the computer experiments in which the solvent is not considered explicitly and is taken into account either via the potential of the average force of interaction of the units or as a continuous viscous medium generating random jolts actually depends on the solution of this kind of problem.

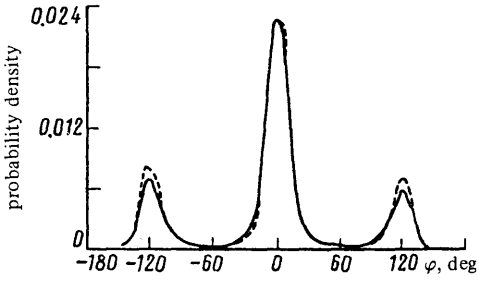


Figure 2. Distribution function with respect to torsional angles ϕ of the central C–C bond for n-butane at 218 K.[32] Continuous line—gas; dashed line—solution in CCL_4; the angle $\phi = 0$ corresponds to the *trans*-conformation.

A system comprising one n-butane molecule and 127 carbon tetrachloride molecules with an overall density of 1.61 g cm^{-3} has been investigated by the MC method.[32] The interaction of the particles was described by the Lennard-Jones potential and the hindrance to the internal rotations around its central C–C bond in butane was described by a three-barrier cosinusoidal potential $V(\phi)$. The transitions between the configurations evolved in conformity with the Metropolis scheme.[15] Analysis of the distribution with respect to the angles of internal rotation showed (Fig. 2) that these distributions are virtually identical for both dissolved and isolated (present in a rarefied gas) butane molecules. In both cases the most probable values of ϕ are 0° and ±120°. The fractions of the *trans*-isomers also proved to be similar: 0.61 and 0.65. Consequently one may say that, within the limits of the accuracy of the calculation, the solvent does not exert an appreciable influence on the conformation of n-butane. Robertus et al.,[33] who modelled a dilute solution of n-butane by the MD method, arrived at the same conclusion.

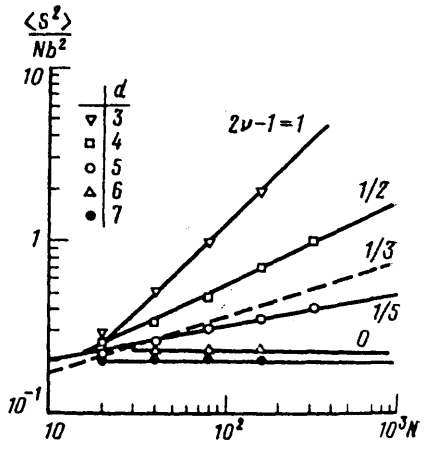


Figure 3. Dependence of the mean square radius of inertia of a charged chain on the number of units for spaces with different numbers of dimensions d.[47] Symbols—MC calculations; continuous lines—calculation based on the Flory theory; dashed line—calculation by the RG method for $d = 5$.

Naturally the calculations for n-butane do not reflect quite adequately the properties of long chains. Computer experiments on the modelling of chains with a large number of units are therefore of special interest. We may note the studies [34–41] in which the MD method has been used. In the first investigations of this kind[34,39] a nine-unit chain ($N = 9$), placed in a cell which also contained $N_S = 855$ solvent molecules, was studied. The interaction between any two particles in the system was described by the Lennard-Jones potential

$$f(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}], \qquad (8)$$

where r_{ij} is the distance between the particles i and j and ε and σ are parameters. We may recall that reduced units are employed in the MD method: the lengths are expressed in units of σ, the rates in units of $(\varepsilon/m)^{1/2}$, and the time in units of $\tau = \sigma(m/\varepsilon)^{1/2}$, where m is the mass (the mass was assumed to be the same for all the particles[34,39]). The chain considered in the above studies[34,39] contained bonds with a rigorously fixed length but the angles between the bonds and the angles of internal rotation were not restricted. The number-average density of the system was $\rho = (N + N_S)L^3 = 0.85$. As a result of averaging with respect to a trajectory whose length was 142τ, the mean square of the distance between the ends of the chain $\langle R^2\rangle$ and the mean square radius of inertia $\langle S^2\rangle$ were found. In addition, the static structure factor $s(Q)$ was calculated for $|Q| \leq 40/\sigma$. For comparison, all the calculations were repeated for the same chain but without taking into account the solvent. It was found that in both cases the average

dimensions of the chains are similar. The functions $s(Q)$ are also virtually identical. Small differences were observed in the region of small $Q \leqslant 1.5/\sigma$ corresponding to units remote from one another. The characteristics of the average form of the polymer coil (i.e. the relations between the orthogonal components of the radius of inertia) also do not exhibit appreciable differences.

Rapaport,[36] who investigated by the MD method freely jointed chains comprising 5, 10, and 20 units immersed in a solvent with $\rho = 0.2$ or 0.3, arrived at analogous conclusions. It was shown that the quantities $\langle R^2 \rangle$ and $\langle S^2 \rangle$ agree satisfactorily with the results of a previous calculation,[42] where the solvent was altogether disregarded.

We may also note a study[41] of the MD modelling of a dense system ($\rho = 0.85$) comprising 246 solvent particles and one ten unit chain with fixed skeletal angles and bonds and with hindered rotation. Calculations taking into account the strong attraction between all the system particles showed that the quantities $\langle R^2 \rangle$ and $\langle S^2 \rangle$ are somewhat greater than in the case of a purely repulsive potential. In our view, this effect is due to the decreased overall pressure in the system.

Since the calculations described refer nevertheless to comparatively short chains, it is doubtful if they fully reproduce the properties of polymers in which the chain length is usually very large. However, this is not so. The use of the MC method in combination with the procedures of the renormalisation group (RG) theory[43] has shown[44] that asymptotic behaviour is attained fairly rapidly for flexible chains with strong volume interactions. Even for $N = 8-16$, freely jointed non-intersecting chains satisfy the relation

$$\langle R^2 \rangle \propto N^{2\nu} \qquad (9)$$

where the critical index $\nu = 0.589 \pm 0.003$, which actually agrees with the limiting value (the best calculation carried out hitherto by the field theory method[45] for $N \to \infty$ yielded $\nu = 0.588 \pm 0.001$; the most reliable experimental result is $\nu = 0.586 \pm 0.004$, which has been obtained[46] for polystyrene with $M_w \leqslant 5.6 \times 10^7$). A criterion of asymptotic behaviour is the inequality $N \gg (b/\sigma)^6$, where b is the chain length and σ the effective rigid chain diameter. For the chains considered in numerical experiments,[34-42] this condition apparently holds, since in all cases $b/\sigma \cong 1$. For this reason, even what are at first sight very short chains should correctly reflect the equilibrium properties of high-molecular-weight polymers.

Thus computer simulation methods have shown that, in dilute solution a low-molecular-weight neutral solvent has only a weak influence on the conformation of a flexible polymer chain for the usual densities and pressures. The interactions of the chain units themselves play a more significant role. The approaches in which the solvent is excluded from explicit consideration in the computer modelling of the equilibrium properties of polymers and the solvent is only considered via the appropriate selection of the interaction potentials between units are therefore fully justified. If the effective potentials are such that the repulsive forces predominate in the interaction and the macromolecule swells, increasing thereby its volume relative to the θ-dimension $R_\theta (R_\theta \sim bN^{1/2})$, it is natural to assume that a thermodynamically effective solvent is modelled. On the other hand, if the coil is compressed relative to R_θ owing to the strong attraction of the units and passes to a globular state, then one models a solvent whose quality is inferior to that of a θ-solvent. Naturally in such a study the effective potentials have the significance of the potentials of the average interaction force, i.e. they determine the change in the free energy and not in the potential energy of the interaction.

Special problems arise in the computer modelling of polyelectrolytes, in which there are long-range electrostatic interactions within the chain. Charged flexible chains containing $N \leqslant 321$ units have been investigated by the MC method in spaces with $d = 3-7$ dimensions.[47] A non-shielded Coulombic potential has been used to describe the electrostatic forces. It was found that the index ν in Eqn.(9) is $\nu = 3/d$. This result is extremely unexpected, because it is in full agreement with the conclusions of the classical Flory theory[48] but shows a sharp discrepancy with the RG treatment,[43] which predicts that $\nu = 2/(d-2)$ for $4 < d \leqslant 6$. This can be seen from Fig.3, where the result of the computer calculation of $\langle S^2 \rangle$ is compared with the RG relation for a five-dimensional space. It may be that in the case of a long-range potential the chain length is insufficient for the complete realisation of the volume effects even with $N \cong 10^2$.

3. Dynamic Properties

In the study of dynamic properties, one usually calculates the diffusion coefficients and various autocorrelation time functions (AF) of the type $C(A, t) = \langle A(0).A(t) \rangle$ characterising under stationary conditions the correlation between the values of the function A considered at time intervals t.

The translational diffusion coefficient D is obtained by integrating the AF for the velocity $C(\mathbf{v}, t)$ by the Green–Kubo formula[22]

$$D = (1/3) \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt,$$

or by the Einstein formula

$$\lim [\langle \Delta r^2 \cdot (t) \rangle]_{t \to \infty} = 6tD + B,$$

where

$$\langle \Delta r^2(t) \rangle = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle$$

is the mean square displacement of the particle during time t and B a coefficient which determines whether the diffusion is more intense or weaker than a Markov process and the angular brackets denote averaging with respect to time and all the particles. The averaging range of T should significantly exceed the relaxation time t_0 of the process considered because the error in the calculation of the normalised AF of the type $\langle A(0).A(t) \rangle / \langle A^2 \rangle$ for a given t is $(2t_0/NT)^{1/2}[1 - \langle A(0).A(t) \rangle / \langle A^2 \rangle]$.

We shall now turn to small-scale and high-frequency movements (corresponding to times $\leqslant 10^{-0}$ s (error in Russian, Ed.) for real systems); information about such systems can be derived, for example, by the dielectric relaxation, polarised luminescence, NMR, EPR, etc. methods. This problem has been studied by the MD method.[37,38,49]

For a better understanding of the polymer effects, we shall consider primarily the simplest "molecule" of anisotropic shape made up of rigidly linked particles ("dumb-bell"), which moves in a liquid made up of non-bonded species. The mean square displacement of the centre of gravity of the dumb-bell is a linear function of t with the exception of a short initial section—the inertial region, where $\langle \Delta r^2(t) \rangle \sim t^2$. As for a homogeneous system, the boundary between the inertial and diffusion regions is determined by the time $t \sim \gamma/m$, where γ is the coefficient of friction of the moving particle. The rotation of the dumb-bell is also described by diffusional laws. This means that the rotational AF bond vectors $\mathbf{b}$ are given by the expression

$$\langle P_l [\cos \theta(t)] \rangle = \exp[-l(l+1) D_R t],$$

where

$$\cos \theta(t) = \mathbf{b}(0) \cdot \mathbf{b}(t)$$

is the cosine of the angle of rotation of b during the time t, P_l is the lth Legendre polynomial, and D_R the coefficient of rotational diffusion. We may note that the foregoing is valid for a bond length $b \gtrsim \sigma$, where the contribution of inertial movements to the relaxation of the AF is small. Otherwise a single characteristic time is insufficient for the description of the orientational AF.

There is a strong relation between the translational and rotational movements of an anisotropic particle in a liquid.[50] This feature can be manifested in spectroscopic experiments. In a dense medium the particle rotates faster the more rapid its translational movement. This correlation can be accounted for by the presence of a local structure in the liquid. For a constant density of the system, the coefficient D for a dumb-bell increases linearly with temperature, which means that the local viscosity of the medium is determined primarily by the free volume.

Overall, analysis of the MD calculations permits the conclusion that the movement of an anisotropic particle in a solvent can by correctly described as the movement of a Brownian particle in a continuous viscous medium. The accuracy of such description increases with increased difference between the masses, dimensions, and shape anisotropies of the given molecule and the molecule of the medium. It must be specially emphasised that the translational movement of a particle and its rotation are, as it were, made up of a large number of small jumps and not of several large jumps. The diffusing particle interacts strongly with its environment under these conditions and its movement is a collective process. This idea was put forward by Frenkel'.[51] The MD method made it possible to elucidate certain fine details of molecular movements in dense media.

The study by the MD method of flexible chains in media made up of particles whose interaction is described by the Lennard-Jones potential [Eqn.(8)] has shown[49] that, for short times $t \lesssim 0.2\tau$, the units move as in the gas phase, while in the range $0.3 < t/\tau < 4$, so long as the displacement Δr remains small compared with the characteristic chain dimension, we have $\langle \Delta r^2(t) \rangle \sim t^{\alpha}$, where $\alpha < 1$. A more detailed study[37] gave $\alpha \cong 1/2$. The manifestation of this unusual motion regime, which is absent for the free particles, is due to the inhibiting effects of skeletal bonds. The presence of branches induces additional inhibition: $\langle \Delta r^2(t) \rangle \sim t^{1/2}/k$, where k is the functionality of the given monomer.[38] We may recall that the $\langle \Delta r^2(t) \rangle \sim t^{1/2}$ relation is predicted by the Kargin–Slonimskii–Rowse model of Gaussian subchains.[43] Naturally, for large values of t, the general diffusion law always holds, although the shift of the monomers is influenced by the chain length: $\langle \Delta r^2(t) \rangle t/N$.

A characteristic feature of the chains with rigid bonds is the increased velocity of the terminal chains compared with the internal chains (the difference is 10–10%).[52] This "hot end" effect is due to the differences in the number of degrees of freedom.

The relaxation of the spatial orientations of the bond vectors of a chain immersed in a solvent has been investigated.[37] Comparison of the results of the MD calculation with the analytical predictions of the viscoelastic Herst–Harris model showed that the relaxation of the mean cosine of the angle of rotation of the bonds [i.e. the orientational AF of the type $\langle \cos \theta(t) \rangle$] takes place in a real chain in virtually the same way as the relaxation of the equivalent quasi-elastic elements in the Herst–Harris model. A rigid chain bond then corresponds to an elastic element of the model and the mean angle between the elements of the viscoelastic model is close to the mean angle between the bonds. In addition, the relation between the mean cosines and mean squares of the cosines of the angles of rotation of the chain bond vectors is similar to the same relation for the individual dumb-bells diffusing in a viscous medium. In other words, the characteristic time of the orientational AF obeys with satisfactory accuracy the expression $t_1/t_l = l(l+1)/2$. However, the orientational AF of the bonds in the macromolecule do not reduce to a simple exponential relation with a single characteristic time t_l and require for their description a fairly broad spectrum of relaxation times. The same conclusion has been reached also in modelling an individual chain by the BD method.[53] This fact is due to the interrelation between different movements in the macromolecule and reflects its chain structure and is not associated with the presence or absence of a solvent.

The general results of the MD calculations can be formulated as follows. The characteristics of the local movements of polymer chains in a low-molecular-weight solvent are close to those manifested in the movement in a continuous viscous liquid. The solvent behaves as a continuous homogeneous medium in relation to the dissolved macromolecule even when the dimensions of the solvent molecule and the chain are comparable. Consequently the MD method confirms the *a priori* postulates which are used in modelling the dynamics of polymers by the BD method, where the medium is regarded at the very beginning as a dense continuum and is not taken into account explicitly but only via the effective coefficient of friction γ in the Langevin equation. Assuming that the chain units move like Brownian particles, it is natural to specify the parameter γ on the basis of preliminary MD calculations. Because of this, there is no need in the BD method to solve the equations of motion for an enormous number of solvent molecules and it is therefore possible to increase significantly the observation time. This is the main advantage of the BD method. It is used, for example, in the study of the conformational *trans–gauche* transitions in polymers with barriers to internal rotation.[53,54] It has been established that the conformational rearrangements occur mainly owing to weakly correlated single barrier $T \rightleftharpoons G$ transitions and their rate is described by the relation $K \exp(-E^*/kT)$, which is close to the Arrhenius relation, where the activations energy E^* differs little from the height of the potential barriers separating the rotational isomers T and G. Cooperative transitions of the type GTT $\rightleftharpoons$ TTG and TTT $\rightleftharpoons$ GTG are observed much more rarely.

We shall now consider the movement of the chain as a whole. The autocorrelation function for the velocity of the centre of gravity of the coil has a complex form: after the rapid decrease to zero (during a time $t \cong 0.2\tau$ for $N = 9$), a region of negative values is observed.[39] This phenomenon is apparently associated with the small number of chain units and can be explained by the fact that the diffusing molecule, having collided with the shell of surrounding particles of the medium, undergoes a kind of "backward reflection". This is possible only when the local environment ("cell") around the molecule considered is retained during a certain period.

It is of interest to compare the AF for the dimensions of an isolated chain and a chain immersed in the solvent. Evidently in a viscous medium the relaxation processes are retarded. Indeed the relaxation times R^2 and S^2 of nine-unit chains suspended in a solvent exceed by more than an order of magnitude the corresponding values for an isolated chain.[39] The vector R connecting the terminal units relaxes most slowly, owing to the necessity for the reorientation of the entire chain. According to Grivtsov

and Mazo,[55] the distance $|\mathbf{R}|$ is an aperiodic function of time, undergoing individual relatively large fluctuations. On the other hand, regular pulsations, whose period increases in direct proportion to N, are characteristic of an isolated chain. An increase of temperature accelerates the decrease of AF. For $t = 10\varepsilon/k$, the AF for a freely jointed chain made up of nine units decrease to zero over a short period $t \lesssim \tau$ corresponding to approximately one vibration period of a pair of particles.[35]

The influence of attraction in a dilute solution has been investigated[41] and it has been shown that allowance for the attraction between all the system particles retards the decrease of the AF for dimensions.

An important question is the study of the dependence on the molecular weight of the characteristic times for the AF describing the relaxation of the polymer coil. The standard approach to the solution of this problem for an isolated chain (without hydrodynamic interaction) consists in using the MC method with its dynamic interpretation. However, in this case it must be emphasised that such calculations based on lattice models yield results which are determined to a large extent by the chosen mechanism of the movement of the chains and frequently lead to various kind of artefacts, including a very marked dependence of the maximum relaxation time of the coils t_m on N: the non-lattice models are therefore preferable.

Using the MC method and the principles of dynamic scaling,[57] it has been shown,[56] in relation to non-intersecting annular molecules, that, as for the equilibrium properties, the asymptotic dependence of t_m on N is attained extremely rapidly (for $N \gtrsim 40$) and the exponent α in the relation

$$t_m \sim N^{\alpha} \qquad (10)$$

is close to 2.2. The same conclusion has been reached in modelling non-lattice non-intersecting chains (N = 5–63) with the aid of the SMART algorithm.[20] It follows from Eqns.(9) and (10) that the formula $\alpha = 2\nu + 1$ holds with satisfactory accuracy. It is known that for Gaussian chains $\alpha = 2$.[43] In addition we may note that the above calculation[56] failed to reveal an appreciable difference in the dynamic behaviour of simple rings and their topological isomers—three-loop knots; for the same N, the times t_m are almost identical.

The role of hydrodynamic interactions can be followed in the MD modelling of solutions or in the study of an individual chain on the basis of the corresponding algorithms based on Brownian dynamics. Calculations by the MD method of the autocorrelation functions for the dimensions of chain ($N \leq 20$) surrounded by the solvent have shown[36] that, for overall system densities $\rho \leq 0.3$, the AF are described by a simple exponential relation $\exp(-t/t_m)$ and the times t_m satisfy Eqn.(10) for $\alpha = 2.2$. t_m increases with increase in ρ.

A fairly unexpected result has been obtained[58] in the modelling by the BD method of hydrodynamic interactions. It was found that the ratio of the chain size R to the hydrodynamic radius of the chain R_H depend both on the coefficient of friction of the unit and on the number of units; on the other hand, in the theory R/R_H = const.[43] It may be that the dependence of R/R_H on N can be accounted for by the insufficient length of the chains investigated ($N \leq 56$).

III. SEMIDILUTE SOLUTIONS

1. Scaling and Computer Simulation

In a dilute solution the polymer coils are separated and only rarely come into contact, while their dimensions at $T > \theta$ are specified by Eqn.(9). The region of a "semidilute solution" $\rho^* \ll \rho \ll 1$, where $\rho^* \sim N/\langle R^2\rangle^{3/2}$ is the critical value of the average density of the polymer units ρ at which the coils begin to overlap, can be determined from general considerations. It follows from Eqn.(9) that $\rho^* \sim N^{-4/5}$, i.e. for high values of N the quantity ρ^* is very small. In a semidilute solution the local density of the units should therefore undergo strong fluctuations. According to modern theoretical ideas,[43] the principal parameter of such a system is the correlation radius of the density fluctuations ξ—the correlation length, i.e. the distance r over which the local density of the units $\rho(r)$ differs from the average value of ρ. The quantity ξ thereby characterises the dimensions of the regions of inhomogeneity in the solution.

The use of the parameter ξ constitutes the basis of an elegant and extremely clear phenomenological description—the so-called blob model. The idea is that, having increased the scale of the study, one passes from the usual formulation of properties in terms of the collective interactions of polymer units to the formulation of the same properties in terms of the interaction of blobs. A blob is defined as a section of the chain (subchain) made up of N_ξ units with the average dimension ξ. In other words, the increase in scale consists in the replacement of the repeating unit whose size is $\sim\sigma$ by a subchain (blob) with the dimension ξ. Since the chains retain their individual properties for scales $r < \xi$, for sections made up of N_ξ units, one can write, by analogy with Eqn.(9), $\xi \sim N_\xi^{\nu}$. On the other hand, for scales $r > \xi$, all correlations vanish by definition. Therefore a chain, which can be imagined to be divided into $n = N/N_\xi$ blobs, has overall the following Gaussian dimensions: $R \sim \xi n^{1/2} \sim N^{1/2}$.

The above data make it possible to express important characterstics such as $\langle R^2\rangle$ and Π (osmotic pressure) in terms of ξ or ρ. When $T > \theta$, we have in the general case for a d-dimensional space

$$\langle R^2\rangle \sim N\xi^{(2\nu-1)/\nu} \sim N\rho^{(2\nu-1)/(1-\nu d)}, \qquad (11)$$

$$\Pi/kT \sim \xi^{-d} \sim \rho^{\nu d/(\nu d-1)}, \qquad (12)$$

where ν enters into Eqn.(9) [or is formulated approximately as $\nu = 3/(d+2)$] and account is taken of the fact that ξ is a decreasing function of the average density:

$$\xi \sim \rho^{\nu/(1-\nu d)} \qquad (13)$$

The above treatment is based on the extremely general hypothesis that in the region of strong fluctuations the thermodynamic and correlation functions are generalised homogeneous functions of their arguments. This hypothesis constitutes the essential feature of the so-called similarity or scaling hypothesis. According to this hypothesis, the transformation of the linear scale $\mathbf{r} \to \lambda\mathbf{r}$ (or, in terms of dynamic scaling, the frequency scale) with an arbitrary similarity parameter λ leads to the situation where the fluctuating physical quantities $A(\mathbf{r})$ should also vary in a similar manner $[A(\lambda\mathbf{r}) \to \lambda^{\Delta}A.A(\mathbf{r})]$ with a similarity exponent Δ_A. On the basis of the phenomenological scaling concept, it is easy to establish a relation between the critical exponents Δ_A, provided that some of

them are already known. An example is provided by the power relations (11)–(13) formulated in terms of a single power exponent ν. However, the calculation of the parameters themselves is a problem for microscopic theory.

One such approach, which takes into account the cooperative interactions in the system, is known as the theory of the mean (or self-consistent) field. The entire classical Flory theory of polymer solutions is based on this approximation.[48] In it, a uniform distribution of the densities throughout the system is assumed, i.e. it is assumed that the local density $\rho(r)$ coincides with the average value of ρ over any distance. In this treatment $\langle R^2 \rangle$ is independent of ρ and formulae (12) and (13) assume the forms $\Pi \sim \rho^2$ and $\xi \sim \rho^{-1/2}$.

The Flory theory proved to be extremely constructive, but, with increase of the experimental accuracy, data conflicting with it began to accumulate. This led to the appearance at the beginning of the 1970's of an alternative approach based on the fundamental postulate of the mathematical isomorphism of two systems: the polymer solution in the region of strong fluctuations and a magnetic material in an external field H near the critical temperature T_c. It has been demonstrated rigorously[43] that there is an unambiguous correspondence between the "magnetic" and "polymeric" variables: $H \leftrightarrow \rho$ and $T/(T - T_c) \leftrightarrow N$ (or N_ξ). The field theory methods, which have been satisfactorily developed for magnetic materials, make it possible to calculate the critical indices at $|T - T_c| \to 0$ (or in polymer terms, $1/N \to 0$) and, by virtue of the analogy indicated between polymers and magnetic materials, these indices are automatically transferred to the polymer theory. In many cases they can be measured experimentally. This is in fact the aim of the computer experiment, whose evident advantage is the possibility of excluding the influence of extraneous factors such as the inhomogeneity of the chemical structure of the specimen and its polydispersity, the association of the macromolecules, etc. In the main, one solves problems designed to discover a measure of the deviation from the classical Flory theory, to refine the limits of applicability of the scaling relations (11)–(13) to the practically important region of the parameters N and ρ, and to test the phenomenological relations between various critical indices resulting from their independent calculation.

The equilibrium properties of semidilute solutions are usually studied on a computer by the MC method. Two characteristic features of the modelling of such systems have been noted. On the one hand, there is the general problem of the modelling of long chains coupled with the need to incorporate a large number of geometrical conditions imposed by the skeletal angles and bonds. Generally speaking, for fixed geometrical parameters, it is not possible to consider the independent movements of an individual chain unit while the remaining chains are stationary, as is done in the Metropolis scheme for a system of "dissociated particles", where only one particle selected at random migrates at each step. For chains with rigid bonds, this type of movement can be organised in three artificial ways. If the chain is modelled by a broken line on a cubic lattice, there is a possibility of jumps of elementary sections in the form of "corners" (fragments made up of two bonds) or "collars" (fragments made up of three bonds); this is the model of Verdier and Stockmayer.[59] In the "slithering snake" algorithm[60] the terminal unit is "torn off" at each step and is reattached in a random manner to the opposite end of the chain. This algorithm is equally applicable to lattice and continuous models. Finally, if the skeletal angles are not fixed, then any internal unit i can be caused to pass to a new state by rotating it by random angle around an imaginary axis connecting the neighbouring $i - 1$ and $i + 1$ units (the Baumgärtner model).[61] In all cases the possibility of the transition between successive configurations is defined by Eqn.(1).

Naturally, the use of smooth potentials (and not δ-functions) for the description of the chain structure makes it possible to abandon artificial mechanisms of motion. The calculations, mentioned above, by means of the SMART algorithm[19–21] lead precisely to this type of model. In addition, without any *a priori* ideas about the mechanism of motion, it is possible to model by the MC method also chains with rigorously fixed bonds (angles), provided that one resorts to correcting algorithms (of the type of SHAKE), which are used in molecular dynamics. However, it is so far not clear whether such schemes have advantages over traditional schemes.[59–61].

On the other hand, by virtue of the fact that in the modelling of semidilute solutions without an explicit allowance for solvent molecules the average density of the test substance in the system is fairly low ($\rho \ll 1$), it becomes possible to use computational methods based on the generation of an *ensemble* of statistically independent configurations, where the chains in each configuration are built up from the beginning to the end by the successive increase in the number of units.[2–4] Polymer solutions constitute an extremely rare example of physical systems for which interesting problems, susceptible to solution by the method of independent samples, exist. Naturally, for $\rho \cong 1$, this method is generally useless. However, in those cases where it can be applied, it is virtually the optimum method.

2. Monodisperse Systems: Concentration Relations

The correlation length. Having specified around each chain unit a sphere with a radius r and having found the number of units $N(r)$ in a volume $V = 4/3\pi r^3$, it is possible to calculate the local density $\rho(r) = \langle N(r) \rangle / V$ after averaging with respect to all the units of the system and with respect to all the configurations generated. For low values of r, the internal density of units makes an overwhelming contribution to $\rho(r)$; in essence, it determines the quantity ξ, which is a result of the numerical solution of the equation $\rho(r) = \rho$, which is satisfied by the condition $r = \xi$.

The concentration variation of ξ has been studied by the MC method for continuous chains with free internal rotation,[62,63] for lattice chains,[64] and for a solution of polyethylene.[65] It has been shown that, for small values of ρ, the quantity ξ is comparable to $\langle R^2 \rangle^{1/2}$ and is naturally independent of ρ. If $\rho > \rho^*$, then ξ diminishes with increase of ρ, which indicates a weakening of the density fluctuations. It has been established[62,63] that for chains in a volume ($d = 3$) and on a plane ($d = 2$), the calculated data are described satisfactorily by Eqn.(13). Thus, for a system of 40-unit chains in the region $0.05 \leqslant \rho < 0.37$, the exponent x_d, which defines the dependence of ξ on ρ in Eqn.(13), was found to be -0.65 ± 0.04 for $d = 3$ and -1.17 ± 0.09 for $d = 2$. For chains on a cubic lattice, the quantity $x_3 = -0.71$ has been obtained.[64]

An important result of the study of Khalatur et al.[65] is the demonstration that ξ is independent of N for $\rho > \rho^*$. This conclusion also follows from de Gennes' theoretical study.[43] When $\rho \to 1$, the quantity ξ approaches the size of the chain unit. It has been established[65] that, for polyethylene chains at a density equivalent to ~0.7 of that of the pure liquid, we have $\xi \cong 0.6$ nm.

These data can be correlated as a result of an experiment[66] where a decrease of ξ from 10 to ~1 nm has been observed in neutron scattering by deuteriated polystyrene for $\rho = 0.01-0.15$. The second value is close to the length of Kuhn's segment, which is 1.7 nm for polystyrene.

A semidilute solution in contact with an impermeable wall has been investigated[67] by the MC method and the distribution of the densities of units $\rho(z)$ in the direction of the normal z to the wall has been calculated. The quantity ξ was found from the condition $\rho(z) = \rho$. Analysis confirmed the power relation (13) and the corresponding exponent was found to be $x_3 = -0.74 \pm 0.15$, which in fact does not differ from the values quoted above. Thus the concentration variations of ξ are virtually the same for different ways of determining it. In all cases the values of x_d found agree well with the theoretical values.[43] In fact, if the fairly accurate approximation $\nu = 3/(d + 2)$ is adopted for the index ν, then we have from Eqn.(13) $x_3 = -3/4$ and $x_2 = -3/2$; in the Flory theory $x_2 = -1/2$.

The correlation length can also be estimated by calculating the intrachain contribution to the static structure factor. Such calculations have been performed by the MC method[68] for 201-unit chains on a lattice. It was found that, for $\rho = 0.344$, the quantity $\xi \cong 10$ when expressed in units of the length of the step in a tetrahedral lattice $b = 3^{1/2}$ and the average number of units in the blob has been estimated as $N_\xi \cong 16$.

Thus computer experiments confirmed the possibility of describing a semidilute polymer solution on the basis of the blob model. It is also significant that the comparatively short chains considered, consisting of several tens or hundreds of statistical segments, correspond to the range of molecular weights of practical importance.

Average dimensions. The dependence of $\langle R^2 \rangle$ on ρ was first investigated[69] by the MC method for continuous chains consisting of 15 and 20 units. It was found that, with increase of ρ, the coils swollen in an effective solvent contract. Analogous conclusions have been reached in a large number of subsequent publications. Sariban et al.[70] also modelled a system under the conditions of a thermodynamically poor solvent at $T < \theta$. For this purpose, they attributed an attraction energy $\varepsilon = -0.5\ kT$ to pairs of units which have approached one another, which led to the contraction of the coils in a dilute solution relative to θ-dimensions. For such a system, the opposite tendency was observed with an increase in ρ: compressed coils became uncoiled and their dimensions approached $\langle R_\theta^2 \rangle$.

A computer study of the functional relation between $\langle R^2 \rangle$ and N showed that,[68] for sufficiently long chains ($N \sim 200$) in an effective solvent, the linear relation $\langle R^2 \rangle \sim N$, corresponding to Gaussian chains and agreeing with Eqn.(11), holds already for $\rho = 0.2$. The same results have also been obtained[71] for a two-dimensional system.

A critical analysis of computer studies of the concentration variation of chain dimensions has been carried out.[72-74] Such a relation can be usefully considered using the scaling variable $X = \rho N^{d\nu-1} \sim \rho/\rho^*$, which provides a measure of the overlap of the coils. It has been noted[73,74] that in the majority of the determinations of the power exponent in Eqn.(11) systems made up of insufficiently long chains have been used. This yielded results differing from the theoretical values. Indeed, for Eqn.(11) to hold it is necessary that the marked inequality $\rho \gg \rho^*$ should obtain. In terms of the variable X, this is equivalent to $X \gg 1$. However, since the range of variation of ρ is always limited, the condition $X \gg 1$ is attained only for very long chains whose computer simulation is difficult for technical reasons. The authors[75] therefore proposed another approach. It follows from scaling considerations that in a general form the quantity $\langle R^2 \rangle$ should satisfy the relation

$$\langle R^2 \rangle \sim N^{2\nu} \cdot Y^{(2\nu-1)/(1-\nu d)},$$

where $Y = \rho/\tau\rho^*$ and $\tau = (T - \theta)/\theta$ is the relative difference between the temperature and the θ point. Clearly, for a fixed value of Y, an improvement in the quality of the solvent (i.e. an increase of τ leads to an increase of the ratio $\rho/\rho^* \sim X$. Consequently, by intensifying the volume interactions, it is possible to achieve the condition $X \gg 1$ without increasing N. In a computer experiment, it is sufficient for this purpose to impart a statistical weight $\omega > 1$ to the units in contact. The corresponding calculations[75] led to the conclusion that, even for comparatively short chains ($N = 40-61$) with $\omega = 0.9$, the power exponent in Eqn.(11) is -0.212 ± 0.050, which is close to the theoretical value of $-1/4$ for three-dimensional systems.[43]

The lattice model of a polyelectrolyte solution has been studied[76,77] by the MC method. An individual non-intersecting chain made up of $N = 16$ or 64 units, some of which carried a unit charge, was placed in a cell with mobile counterions. Each counterion also had a unit charge and was regarded as an occupied lattice site. The interaction between the charges was described by a non-shielded Coulombic potential. Using the local jump method,[59] the authors investigated the dependence of the chain size on the fraction of charged units p_e and the average density of units, which was varied by altering the volume of the computational cell for fixed values of the remaining parameters. The calculation showed that the chain swells with increase in p_e. Consequently the environment made up of counterions, arising around the chains, cannot compensate for their electrostatic repulsion. This effect is most pronounced in a dilute solution (i.e. at a low ionic strength), where the total electrostatic energy is positive and the form of the polyion is close to being rod-like. The decrease in cell size modelled the increase in ionic strength. When the Debye radius is less than the chain radius R, the total electrostatic energy becomes negative and the polyion assumes the form of a coil. Under these conditions, the role of electrostatic interactions is insignificant compared with the "usual" volume interactions.

Interaction of coils and osmotic pressure. In dilute solution, the virial expansion

$$\Pi/kT = C/N + A_2C^2 + \ldots \qquad (14)$$

where $C = \pi\sigma^3\rho/6$ and A_i is the ith virial coefficient, holds for Π. On the other hand, one can write for an arbitrary concentration[22]

$$\frac{\Pi V}{mkT} = 1 - \frac{1}{6kT} \cdot \frac{mN^2}{V} \int_0^\infty 4\pi r^2 g(r) \frac{\partial f(r)}{\partial r} r\,dr, \qquad (15)$$

where m is the number of chains in the system, $g(r)$ is the "intermolecular component" of the radial distribution function of the unit, and $f(r)$ is the interunit potential.

The temperature variation of A_2 has been investigated[78,79] for lattice chains and the inversion of the sign of A_2 (the θ point corresponds to the equality $A_2 = 0$) was considered. It was found that the critical energy for a single contact between units $\varepsilon_0 \sim 1/T$, for which $A_2(\varepsilon_0) = 0$, depends on the chain length and differs for each N from the value of ε_0 at which the swelling of the coils ceases.[80] The quantity ε_0 approaches its limiting value ε_0^∞ as $\varepsilon_0(N) = \varepsilon_0^\infty(1 - N^{\theta-1})$.[80,81] Thus, in the case of finite chains one should speak of a θ region rather than of a θ point. We emphasise that the concept of the θ region was first introduced precisely on the basis of the analysis of the results of a computer calculation[82] and Khokhlov subsequently achieved a rigorous physical justification of this concept.[83]

The quantities Π and A_2 are linked directly to the pair correlation function for the interaction of coils $G(h)$, which determines the probability of finding them at a distance h from one another. The function $G(h)$ was calculated by the MC method.[84-86] The fundamental result of the studies of Khalatur and co-workers[85-87] has been the demonstration of the fact that, in an effective solvent, the probability of encountering conformations with a marked overlapping of the coils is significantly different from zero even on extrapolation to $N \to \infty$. On the other hand, the classical Flory–Krigbaum theory[48] predicts a zero probability of such states for chains with an excluded volume. An explanation of the results of the computer experiments and of the deficiencies of the Flory–Krigbaum theory has been given on the basis of simple scaling considerations.[85,86] These conclusions were later confirmed more rigorously using the renormalisation group method.[88] Sharp differences from the Flory–Krigbaum theory are also observed for the θ region.[4,89]

The concentration variation of Π has been investigated for an athermal system[90-93] also taking into account the interunit attraction.[94] We may note that, when the units are modelled by rigid spheres with a diameter σ, then Eqn.(15) transforms into the simple expression

$$\Pi V/mkT = 1 + 4NCg(\sigma),$$

where $g(\sigma)$ is the value of $g(r)$ at the point of contact for $r = \sigma$ and the product $C.g(\sigma)$ gives the average number of contacts referred to one unit.

Calculations for non-lattice chains with $N \leq 40$ showed[93,94] that the relation $\Pi \sim \rho^x$, where $x = 2.44$, holds in an effective solvent. From Eqn.(12) with $d = 3$, we have $x_3 = 9/4$. On the other hand, in the Flory–Huggins theory[48] $\Pi \sim \rho^2$. The difference is due to the fact that the Flory–Huggins theory[48] neglects the important correlation effects arising due to the chain-to-chain binding. For the osmotic isothermal compressibility, it was found[94] that $\rho^2\beta_T \sim \rho^{-0.3}$, while in the case where correlations were not taken into account we have $\rho^2\beta_T = \text{const}$.

The possibility of describing the relation $\Pi(\rho)$ on the basis of the integral equations of the theory of liquids (the Percus–Yevick and hyperchain approximations) has been considered.[95] It was found that in the region $\rho > \rho^*$ these approximations give an unduly low pressure compared with the computer calculations. Two-dimensional systems have also been simulated.[92,93] $\Pi \sim \rho^{3.07}$ has been obtained[93] for an athermal system. It follows from Eqn.(12) that $\Pi \sim \rho^3$. In addition, in the same study it was discovered that $\Pi \sim \xi^{-d}$.

Thus the computer simulation of semidilute solutions of flexible chains in an effective solvent generally confirms the validity of the scaling method and yields critical indices close to those obtained in modern theories. On the other hand, a systematic deviation from classical ideas has been observed.[48]

3. Polydisperse Systems

Real polymer systems almost always exhibit a particular degree of polydispersity. The role of this factor has been analysed using scaling relations.[96] The behaviour of a flexible chain made up of N_1 units surrounded by units having the same chemical composition but made up of shorter chains with N_2 units has been considered. It was established that, when $N_2 \lesssim N_1^{1/2}$, then, in an effective solvent with an overall density $\rho > \rho^*$, the size of long chains $R_{1,2}$ in a mixture with short chains should increase compared with the size R_1 of the same chains at the same density but in the absence of short chains. The relative swelling coefficient

$$\beta = \langle R^2_{1,2}\rangle / \langle R_1^2\rangle$$

depends both on the ratio of N_1 and N_2 and on the density ρ.

Continuous non-intersecting chains with free internal rotation have been studied[97] by the MC method. In the first place the concentration variation of $\langle R_1^2\rangle$ was obtained for a monodisperse solution of 61-unit chains. Some of these chains (50%) were then replaced by shorter chains with $N_2 = 5$. The density was then defined as $\rho = (m_1N_1 + m_2N_2)/V$, where V is the volume of the computational cell and m_1 and m_2 are the numbers of chains of different kinds in the cell. In a monodisperse system, the quantity $\langle R_1^2\rangle$ also decreases with increase of ρ. The contraction of the coils has been observed also in a two component system made up of chains of two kinds. However, the decrease of $\langle R^2_{1,2}\rangle$ begins later than that of $\langle R_1^2\rangle$ (for $\rho/\rho^* \gtrsim 2$). It has been shown that, for the same density, $\langle R^2_{1,2}\rangle > \langle R_1^2\rangle$. Consequently the relative swelling coefficient $\beta > 1$. In other words, the replacement of some of the long chains by short chains entails the swelling of the longer chains, which is equivalent to an improvement in the quality of the solvent for them. Naturally, with increase of ρ, the absolute size of the coils in an effective solvent always diminishes, although the ratio β increases in proportion to ρ. According to Pletneva et al.,[97] such an increase continues for the system investigated up to $\rho \cong 0.2$, after which β virtually ceases to vary.

The computer modelling of a polydisperse system has also been carried out using the SMART algorithm.[98] A mixture of flexible chains with $N_1 = 70$ and $N_2 = 5$ (the cell with $\rho = 0.3$ contained ten 5-unit chains and one 70-unit chain) and it was found that the quantity $\langle R^2\rangle$ for a "trial" 70-unit chain in a medium made up of short chains increases by a factor of 1.1 compared with the homogeneous system, which is close to the results of Pletneva et al.[97] The concentration variation of β has not been investigated.[98]

It is noteworthy that the results of computer calculations considered above[97,98] agree qualitatively with the experimental data[99] for neutron scattering by mixtures of polydimethylsiloxanes.

IV. POLYMERIC LIQUIDS

1. Conformational Structure of Macromolecules

In the computer study of macroscopically isotropic (liquid, amorphous) polymers two questions are usually considered: (1) in what way does the local structure of a polymeric liquid made up of macromolecules with a large number of chemical bonds differ from the structure of a simple low-molecular-weight liquid and (2) how the chain conformation in the block differs from that in a dilute solution.

In most investigations of this field by the Monte Carlo method calculations have been made of the dimensions of the macromolecules represented by the simplest general models on lattices or in continuous space. Summarising the results obtained, one may say that, regardless of the model employed, the dimensions of flexible non-interacting chains in a block with a density $\rho \gtrsim 0.6$ are close to the θ dimensions. The dependence of $\langle R^2\rangle$ on the molecular weight is the same as for immaterial Gaussian chains, i.e. $\nu = 1/2$ in Eqn.(9). These conclusions confirm the so-called "Flory theorem".[48] This type of behaviour is a consequence of the fact that, for $\rho \cong 1$, the local density of the units hardly differs from the average value for the systems: the density fluctuations are therefore small and the treatment within the framework of the approximation of an average molecular field becomes valid.

Since the end of the 1970's, numerical experimental methods have been used vigorously in the study of more complex systems: liquid n-alkanes and polyethylene. An undoubted advantage of such systems is the possibility of a direct comparison of the calculated results with experimental data. On the other hand, the combination of computer methods, physical experimental methods, and analytical theory leads to the best understanding of the problem under consideration.

The MC method has been used[100–105] for the modelling of hydrocarbon chains in the melt. For each molecule of the system, account was taken of the chemical structure and of the hindrance and interdependence of the internal rotations. The interaction of chemically non-bonded groups was described by the Lennard-Jones potential [Eqn.(8)], whose parameters were selected on the basis of experimental data. Chains containing between 8 and 30 carbon atoms were studied;[100,101] longer chains (up to C_{101}) were examined in other studies.[102–105] The calculations showed that, for a density $\rho \gtrsim 0.7$ (relative to the density of the pure liquid), the chain sizes reach a constant value and depend only on the temperature and chain length but not on ρ. The mean square radii of inertia $\langle S^2 \rangle$ found for the melt are compared in Fig.4 with the corresponding values measured experimentally by the small-angle neutron scattering method.[106–108] In all cases an entirely satisfactory agreement between the results is observed. On the other hand, the values of $\langle S^2 \rangle$ for the chains in the block are close to the values of $\langle S_\theta^2 \rangle$ calculated analytically by the method of generating matrices for isolated chains without volume interactions. Consequently hydrocarbon chains in the melt are coiled up to form statistical coils. It is important to note that two series of independent calculations, i.e. those of Vacatello et al.[100] and Avitabile and Tuzi,[101] on the one hand, and those of Khalatur and co-workers,[102–105] on the other, carried out by means of different algorithms and on different computers, yielded virtually identical results.

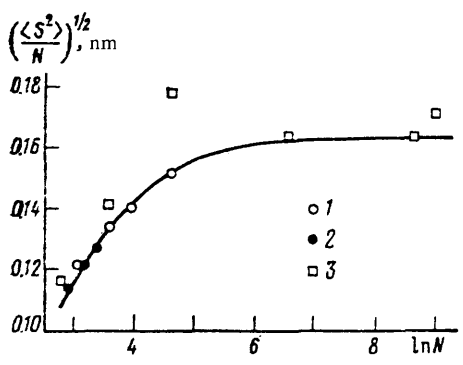


Figure 4. Dependence of $\langle S^2 \rangle$ for polyethylene chains in the melt on the number of carbon atoms N: 1) and 2) results of MC calculations from Refs.102–105 and 101 respectively; 3) experiment;[106–108] continuous curve—analytical calculation.

The problem of the mechanism of the transitions between the *trans*(T)- and *gauche*(G)-rotational isomers occupies an important place in the computer modelling of polymers. Naturally, for the solution of this problem it is necessary to consider realistic models. In this respect, the polyethylene oligomers are again the most convenient. The results of the molecular-dynamic calculations for liquid n-butane and n-decane[109–111] can be summarised as follows.

For liquid n-butane near the boiling point (292 K), a slightly increased fraction of the *gauche*-isomers (p_G) with respect to the C–C bonds is observed as compared with the gas phase: $p_G = 0.46$ in the liquid and $p_G = 0.34$ in the gas. The average $T \rightleftharpoons G$ transition time is ~10 ps. Modelling of liquid n-decane (27 molecules at 481 K) over 19 ps showed[111] that the average time interval Δt between conformational transitions is ~2.1 ps. The fractions of the *gauche*-isomers with respect to different C–C bonds and the times Δt are listed in Table 1. The relaxation of the chain as a whole takes 2–4 ps. This period is sufficient for the occurence of ~15 *trans–gauche* transitions. It has been shown[111] that the local conformation of n-decane is almost fully determined by intramolecular interactions.

More detailed calculations of the rotational-isomeric composition have been performed for liquid polyethylene oligomers by the MC method.[103,104] Not only the contents of the individual T- and G-isomers but also the contents of the various combinations of the *TT*, *GG*, *TG*, *TTT*, etc. types have been determined. We may note that it is only comparatively recently that we have learnt to extract such data from infrared and Raman spectra. Comparison of the results of computer modelling[103,104] for liquid C_{21}, C_{51}, and C_{101} hydrocarbons with infrared spectroscopic data and the results of analytical calculation for unperturbed chains has shown a good quantitative agreement in all cases. This demonstrates that the local conformational structure of flexible chains in the block also differs little from the structure of a Gaussian coil.

The factors enumerated above constitute the most convincing evidence for the validity of the "Flory theorum" which has been produced by computer experiments.

2. Correlation in Liquid Polymers

We have already spoken of the correlation radius for density fluctuations; according to the results of the MC calculation,[65] $\xi < 1$ nm for liquid hydrocarbons. Calculations of the radial distribution functions[100] also show that $g(r) \cong 1$ at $r \gtrsim 0.7$ nm. The first $g(r)$ maximum in a hydrocarbon liquid, corresponding to the first coordination sphere, has been found at 0.4 nm, which agrees well with experimental X-ray diffraction data. In addition, the correlation function for the orientations of intermolecular pairs of C–C bonds has been determined[100] and it has been found that the orientational correlation disappears completely already at distances greater than 0.5 nm. An analogous result has been obtained[112] by the MD method for polyethylene having a density of 774 kg m^{-3}. At $r \lesssim 0.5$ nm, a weak tendency towards a perpendicular arrangement of segments has been observed. It has been established that even at $\rho > 0.5$ and even more so in the block state the polymer coils overlap almost completely.[87,113]

The question of the interpenetration of the coils on a plane has not been fully elucidated as yet. The available results of computer calculations are not unambiguous. Baumgärtner's data[114] indicate a tendency of two-dimensional coils towards segregation, which agrees with the hypothesis put forward by de Gennes.[43] However, this conclusion conflicts with other computer experiments[67,115] and theoretical studies[85,86] within the framework of the scaling method.

The relaxation behaviour of hydrocarbons in the melt has been investigated by the MD method.[109–111] Calculations[111] of the autocorrelation functions for the coil sizes in liquid n-decane have shown (Fig.5) that the AF for S^2 and R^2 decrease to zero over a period of ~1.5τ (2–3 ps). Consequently, despite the high viscosity of the medium, the coil sizes relax fairly rapidly. When the strong attraction of

the units is taken into account in the calculation, the rate of decrease of the AF diminishes[116] but to a much lesser extent than for a chain in a dilute solution. It is of interest to note that the AF calculated[111] by the MD method could be reproduced almost quantitatively by the method of Brownian dynamics for an individual chain with an appropriate choice of the coefficients of friction for the methylene group.[28] This result is also illustrated in Fig. 5. Naturally, the simulation of a dense system by a single macromolecule in the BD method is not suitable for the investigation of phenomena associated with topological effects arising owing to the intertwining of the chains in the liquid polymer. Such phenomena include the diffusion of the chains, which will be considered in the next Section of this review.

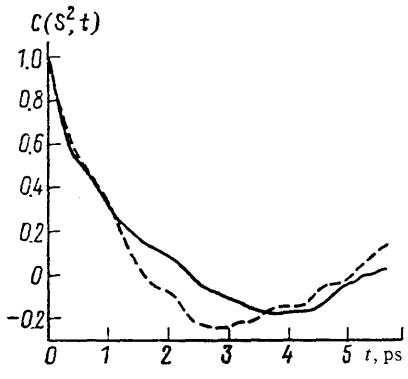


Figure 5. The autocorrelation function of the square of the radius with inertia of the n-decane chain.[111] Continuous curve—MD calculation for the melt; dashed curve—calculation by the method of Brownian dynamics for an individual chain.

Table 1. The fractions of the *gauche*-isomers relative to C–C bonds and the *trans-gauche* conformational transition times in liquid n-decane at 481 K.[111]

No. of the C–C bond in the chain	p_G	Δt, ps
2 and 8	0.45	1.9
3 and 7	0.36	2.1
4 and 6	0.34	2.4
5	0.44	1.7

Naturally, in contrast to low-molecular-weight liquids, in liquid polymers there are correlations of a special kind due to the strong (chemical) bonds between neighbouring units in the chain. The role of these correlations can be traced by calculating the Van Hove spatial-temporal correlation function $G(r, t)$ (its Fourier transform defines the differential coherent scattering cross-section).[22] This function can be conveniently divided into two parts:

$$G(r, t) = G_d(r, t) + G_s(r, t),$$

where $G_d(r, t)$ is the density of the probability of observing any other species at time t and a distance r from the given species, while $G_s(r, t)$ is the density of the probability of observing the same species. We may note that $G_d(r, t)$ describes the evolution of the radial distribution function in time and $G_d(r, 0) \equiv g(r)$. The calculations of G_d and G_s were performed by the MD method for a system made up of 20 flexible 16-unit chains at $\rho = 0.8$.[117] The interaction of the units was described by the repulsive component of the potential defined by Eqn. (8). Fig. 6 presents the functions $g(r)$ and $G_d(r, t)$ at different times. The high first peak (with a height of ~11) on the $g(r)$ curve at $r = 1$ corresponds to the closest (bound) monomers in the chain separated by bonds of different lengths. The subsequent maxima correspond to different coordination shells. In the region $r > 4$ the oscillations in the $g(r)$ have almost completely decayed, which is also characteristic of simple low-molecular-weight liquids.[22] Thus the principal specific features of the equilibrium structure of a liquid polymer consist in the presence of an intense "valence" peak on the $g(r)$ curve.

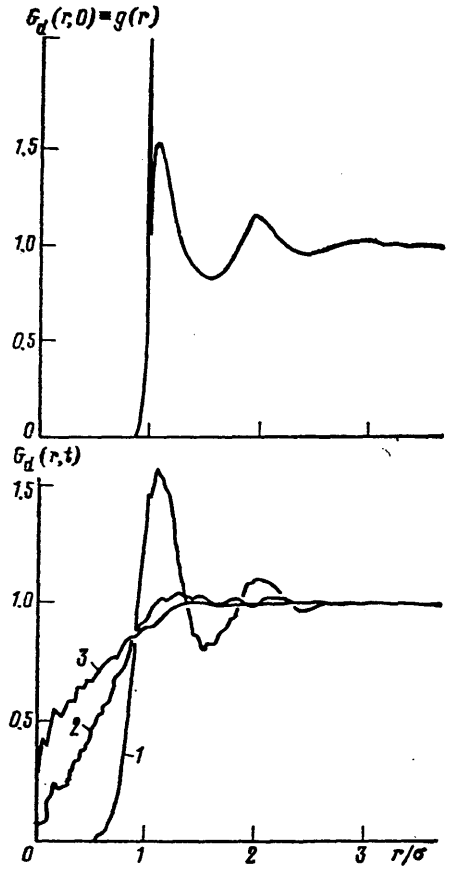


Figure 6. Radial distribution function of the density of the particles and the Van Hove function for a polymeric liquid at different times t: 1) 0.2τ; 2) τ; 3) 2τ.

It might have been expected that many bonds in the chains should influence strongly the dynamics of the decomposition of the pair density correlations. However, Fig. 6 showed that, even for $t > 0.2\tau$, a barely perceptible trace remains of the "valence" peak on the $G_d(r, t)$ curve. With increase of t, other peaks spread and gradually disappear. Nevertheless, even at $t \cong \tau$, the short-range order cell, made up of particles in the first coordination sphere, is appreciable.

The region of forbidden volume persists for an even longer period for low values of r. However, during a period $t > 4\tau$, the initial $G_d(r, t)$ structure decomposes to a large extent and at $t \gg \tau$ we have $G_d(r, t) = 1$ for all distances, i.e. any relative positions of the particles are equally probable. The autocorrelation function $G_s(r, t)$, describing the self-diffusion of the particles, then obeys the Gaussian law.

3. Reptational Movement

De Gennes[118] proposed a heuristic model, which has been called the "reptation model", for the description of the diffusion of flexible chains in dense media. The movement of the chain can be clearly represented using the concept of an effective tube: it is assumed that at any instant each chain is, as it were, enclosed in a "tube" made up of the steric hindrance generated by other chains in the system. The macromolecule diffuses within this tube as a result of local conformational rearrangements—"defects", which migrate preferentially along the chain contour. Such low-scale (in fact one-dimensional) movement is the basis of the reptation model.

One of the maximum characteristic times of the process is $t_R \sim N^3$, during which the chain moves along the tube over a distance of the order of its contour length. At $t \sim t_R$ the movement of the chains is described by the relation $\langle \Delta r^2 \rangle \sim (t/N)^{1/2}$. For times much shorter than $t_R (t \leq t_R/N)$, when the average displacement of any unit $\langle \Delta r^2 \rangle^{1/2}$ is comparable to the effective tube diameter d_T, a special "local reptation" regime should be observed, in which $\langle \Delta r^2 \rangle \sim t^{1/4}$. Finally, for very short times t, the movement of the unit is controlled solely by the intrachain bonds and not by intermolecular interactions, which corresponds to the usual Rouse model, i.e. $\langle \Delta r^2 \rangle \sim t^{1/2}$.

The experimental observation of reptations in liquid polymers is extremely difficult. For this reason, there are as yet no direct unambiguous data confirming or disproving the postulated reptation mechanism. In a series of recent studies,[68,98,119–123] an attempt has been made to observe reptation by the dynamic MC method.[59,61] However, in the modelling of melts this could not be done. In our view, the failure can be accounted for by two causes. Firstly, in the above studies insufficiently dense systems ($\rho < 0.7$) were considered. Since $\langle \Delta r^2 \rangle^{1/2}$ should be close to d_T for the manifestation of reptational movement, it follows that, when account is taken of the estimate $d_T \cong (\sigma\rho)^{-1/2}$ (σ is the diameter of the monomer), it becomes clear that for low ρ, it is difficult to reproduce the required regime in a numerical experiment. Secondly, in modelling polymers by the dynamic MC method, the movement of the macromolecule is achieved as a result of successive rearrangements of short sections of the chains. It is then found that, for chains with volume interactions and rigid bonds, the rate of migration of units along the chain contour is very low. The reptation mechanism is therefore hardly realised. This has been confirmed by the results of a study[121] where the reptational movement has been observed only after assuming the overlapping of the monomers within the same chain. For this reason, one cannot regard as satisfactory also the calculations[122] for an individual macromolecule without exchange interactions, moving within a regular network of obstacles modelled by a regular cubic lattice. Furthermore, the appearance of reptational movement in a medium with regular obstacles is in general doubtful.

It has been reported[68,98,119,120] that it has been possible to observe a transition from the Rouse regime ($\langle \Delta r^2 \rangle \sim t^{1/2}$) to the reptational regime ($\langle \Delta r^2 \rangle \sim t^{1/4}$) after the movement of all the chains in the melt has been "frozen" with the exception of one trial chain. We should like to draw attention to the lack of justification of this conclusion. In fact, in the random appearance of a "frozen network" there is an extremely high probability that a mobile chain is incorporated in a cell closed on all sides (and not in a tube open at two ends), which naturally causes a sharp retardation of the movement.

The reptation of chains in the melt has also been investigated by the MD method.[117] This method is free from the above disadvantage characteristic of the MC method and it therefore provides a more objective description of the dynamic behaviour. The mean squares of the displacements of the units $\langle \Delta r^2 \rangle$ and the orthogonal components of the movement along the chain contour (the tangential component $\Delta \mathbf{r}_\parallel$) and across the contour (the normal component $\Delta \mathbf{r}_\perp$) have been considered[117] for a dense system of 20 flexible chains ($N = 16$, $\rho = 0.8$). Clearly

$$\langle \Delta r^2 \rangle = \langle \Delta r_\parallel^2 \rangle + 2\langle \Delta r_\perp^2 \rangle$$

and the ratio

$$Q = \langle \Delta r_\parallel^2 \rangle / \langle \Delta r_\perp^2 \rangle$$

is therefore always unity for isotropic movement. In order to make a comparison with the melt, an individual chain has also been considered.[117] The calculation showed that, owing to the presence of rigid bonds, the movement of the units of an individual chain in the tangential direction is suppressed and the normal component predominates, so that always $Q \leqslant 1$. An analogous behaviour is characteristic also of chains in the melt for short times $t \leqslant \tau$. The dynamic properties are then determined solely by the chain structure of the macromolecules and not by their interaction. However, for $t \geqslant 1.2\tau$, where each unit in the melt has sufficient time to traverse a fairly long distance $\sim d_T$, the obstacles offered by the surrounding chains, which arise during the movement in the transverse direction, force the units to migrate predominantly along the chain contour, as a result of which $Q > 1$. This picture can be readily traced in Fig. 7. Naturally, for very long times, the movement must be isotropic.

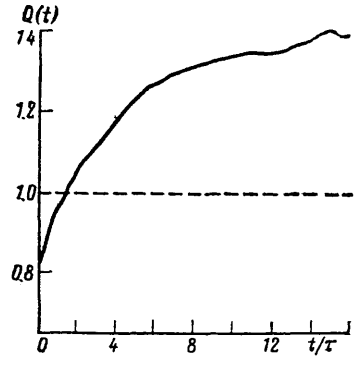


Figure 7. Time variation of the function $Q(t)$ defining the ratio of the shifts of the polymer chains along and across the chain contour. The calculation was performed by the method of molecular dynamics for a dense polymeric liquid.[117]

Thus a dynamic numerical experiment has shown that in a polymeric liquid there exists a preferential type of movement of the chain units along the chain contour. This

movement is solely determined by a specific interchain interaction and can be identified with local reptations in the melt. From the general standpoint, this situation is fairly unusual: in a system having an isotropic structure, there exists a local anisotropy in the movement of the particles.

V. PARTLY ORDERED SYSTEMS

1. Liquid Crystal Polymers

The fields involving the practical application of polymeric liquid crystals have expanded sharply in recent years and new prospects have arisen for their further application. These factors stimulated theoretical studies of the conditions governing the appearance and physical properties of liquid crystal systems.

The possibility of transition to a liquid crystal phase is associated with the rigidity of the polymer chain, characterised by the statistical Kuhn segment A, rather than by its great length. If $A \gg \sigma$ (σ is the chain diameter), then, under certain conditions, orientational ordering may take place. Polybenzamide, poly-(benzyl glutamate), and cellulose esters are typical examples of mesogenic macromolecules for which $A \gg \sigma$.

There exist two main approaches to the theoretical description of the orientational ordering of macromolecules: the Onsager method,[124] in which the virial expansion of the free energy of a rarefied gas comprising rigid rods is employed, and the Flory method,[125] based on the lattice model of the polymer. The present development of the Onsager theory has been described by Khokhlov and Semenov.[126]

Unfortunately, an analytical treatment can be rarely continued until numerical results are obtained, which applies particularly to the most interesting semirigid chains, for which L is frequently comparable to A. The computer simulation of such systems is therefore evidently essential.

Equilibrium properties. The question of the conditions governing the transition to the liquid crystal state and the conformational changes in the orientational ordering of semirigid chains was first solved by the MC method.[127] Chains with free internal rotation, consisting of N rigid units with a single diameter σ connected by bonds of unit length at a specified angle α, were considered. The angle α was chosen so that the local asymmetry parameter A/σ was 57.7 and the criterial Flory parameter f was 0.074, which reproduced the value of f for the nitrocellulose chain.[13] The results of the calculation for 40-unit chains are presented in Fig.8, which illustrates the dependence of the quantity $\langle R^2 \rangle$ and the orientational order parameter $\eta = [(3 < \cos^2\gamma) - 1]/2$ (γ is the angle between the vector **R** connecting the ends of the chain and the director of the specimen) on the number-average density ρ. Evidently, for low values of ρ, the parameter $\eta \cong 0$, i.e. the system is isotropic. Appreciable changes in η and $\langle R^2 \rangle$ begin only at $\rho \geqslant 0.1$, where these quantities exhibit a rapid increase. The increase in η shows that the system passes to a liquid crystal state (of the nematic type). The transition is accompanied by an increase in the length and rigidity of the chains. For $\rho \to 1$, it was found that $\langle R^2 \rangle \to L^2$. This effect constitutes a fundamental difference between the behaviour of semirigid and flexible chains. For comparison, Fig.8 illustrates the concentration variation of $\langle R^2 \rangle$ calculated for the same system of 40-unit chains but exhibiting a high flexibility ($\alpha = 90°$ and $A/\sigma = 1$). In this case the picture is completely reversed: with increase in ρ, the order parameter does not change and is close to zero, while $\langle R^2 \rangle$ tends to $\langle R_0^2 \rangle$. It has been shown[127] that the order effects, observed in the system of semirigid macromolecules, depend only slightly on the attractive forces. As for low-molecular-weight liquid crystal systems, the repulsive component of the interaction potential plays the main role.

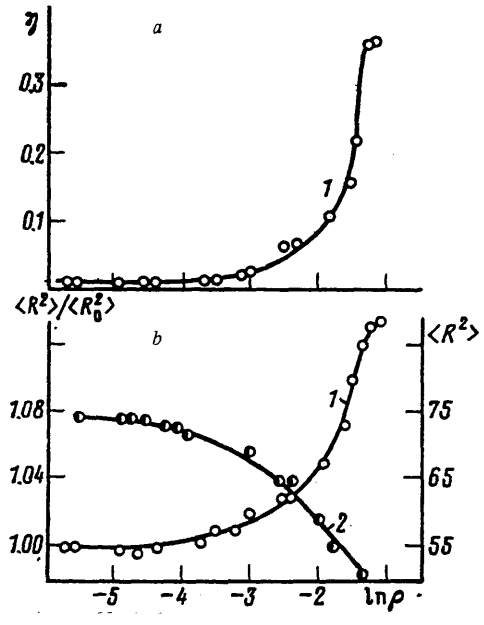


Figure 8. Dependence of the order parameter (a) and average chain dimensions (b) on the density: 1) system of semirigid chains (the quantity $\langle R^2 \rangle$ is expressed relative to the size of an isolated chain); 2) system of flexible chains.[127]

The results of the computer experiment[127] can be compared with theoretical predictions.[126] For the model considered by Pletneva et al.,[127] the ratio $L/A = 0.67$ and the critical density at the transition point ρ_c, estimated from the maximum in the derivative $d\eta/d\rho$, was found to be 0.23 (under these conditions, $\eta_c = 0.37$). The theory[126] yielded $\rho_c = 0.26$ and $\eta_c = 0.41$ for the same L/A ratio. The agreement with the computer calculation is clearly extremely good. We may note that the Flory theory[125] yields a low critical density for the model investigated.[127]

The theoretical study[124,126] was based on the second virial approximation and its applicability is therefore restricted to the range of comparatively low polymer concentrations. On the other hand, the lattice model[125] describes the ordering in concentrated systems. Nevertheless, MC calculations[128] for the two-dimensional lattice model with $\rho = 0.952$ revealed significant deviations from the Flory theory. Recently the same workers[129] carried out an analogous calculation for a three-dimensional system of chains ($N = 20$) on a cubic lattice (441 chains with $\rho = 0.952$). The rigidity of the chain was regulated by the parameter $\Delta\epsilon$, which determines the extent to which the forward step on the lattice (the *trans*-isomer) is preferred to the sideways step (the *gauche*-isomer). Approximately 3.5×10^9 configurations were generated for each $\Delta\epsilon$ using the "quasi-reptation" algorithm.[60]

The results of the calculation of η and of the average fraction of the *gauche*-bonds p_G are presented in Fig. 9. These values can also be found within the framework of the lattice theory,[125] according to which the critical transition temperature $kT/\Delta\varepsilon_c = 0.56$ for $N = 20$ in the absence of unoccupied sites on the lattice. Calculation by the MC methods has shown that, with decrease of $kT/\Delta\varepsilon_c$ (i.e. with increase of the rigidity of the chains), there is a sharp transition at the point $kT/\Delta\varepsilon_c = 0.64$: the chains are almost completely uncoiled and ordered. Evidently, in the three-dimensional case there is a satisfactory correlation between the critical values of $kT/\Delta\varepsilon_c$ obtained theoretically[125] and in the computer experiment. On the other hand, the computer calculation reveals the phenomenon of hysteresis: the reverse transition from the ordered to the disordered states takes place at a different point $kT/\Delta\varepsilon'_c = 0.68$. The description of this behaviour is outside the framework of the theory.[125]

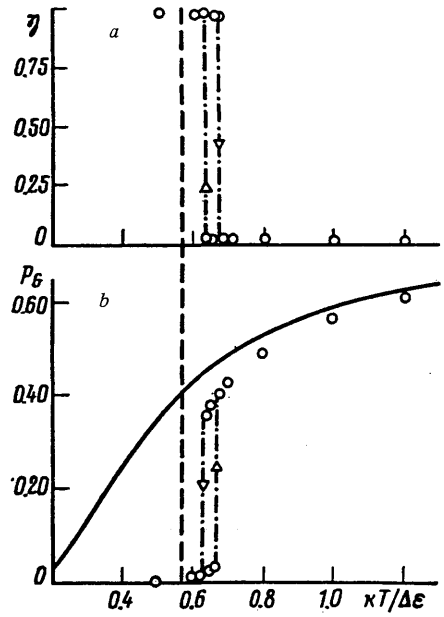


Figure 9. Dependence of the order parameters (*a*) and the average fraction of *gauche*-bonds (*b*) on the reduced temperature for the lattice model of a liquid crystal. Symbols—calculation by the Monte Carlo method (the arrows indicate the direction of the forward and reverse transitions); continuous curve—calculation based on the Flory theory; the dashed line indicates the critical transition temperature in the Flory theory.[125]

It must be emphasised that, in the examples described above, the rigid chains were ordered without any involvement of the attraction forces, solely as a result of packing effects. In a number of instances packing effects can cause the orientational ordering of flexible chain polymers. For this purpose, it is sufficient to restrict the mobility of the chains in space. Computer experiments have shown[130–132] that flexible chains "tied" by one end to an impermeable surface (for example, as a result of the strong adsorption of the terminal polar group or chemical "grafting") are capable of orientational ordering solely as a result of the steric hindrance, which depends on the degree of surface coverage. Another possibility for the transition of flexible chains to an ordered state is associated either with the presence of external orienting fields or with the anisotropy of the intermolecular interaction forces.[133]

Dynamic properties. There have been few studies on the modelling of partly ordered polymer systems by the MC method. Pershin and Skopinov[134] examined a two-dimensional system of rigid five-centre molecules and observed a tendency towards the formation of short-lived associated species (clusters) in which the degree of local order was higher than the average for the system. The association of molecules following their mutual approach is caused, according to the authors, by potential barriers preventing the shear displacement and stabilising a parallel configuration.

The dynamics of the behaviour of molecules having the form of infinitely rigid rods has been studied.[135] Although the cross-sectional area of the rods was assumed to be zero, they could not cross each other. Depending on the reduced density $\rho^* = NL^3/V$ (where N is the number of rods with a length L in a volume V), the AF for the rates of self-diffusion coefficients

$$D = (D_{\parallel} + 2 \cdot D_{\perp})/3,$$

where $D_{\parallel}$ and $D_{\perp}$ are diffusion coefficients in the longitudinal and transverse directions, were calculated. It was shown that, during the period between two collisions, the movement is free and not diffusional. For low values of ρ^*, the transport properties are described satisfactorily by the kinetic Enskog theory.[22] However, for $\rho^* \geqslant 8$, this treatment ceases to be valid. It was found for this range of densities that the rotational diffusion coefficient of the rod decreases as $(\rho^*)^{-2}$ or as L^{-6}, in conformity with the theory of Doi and Edwards.[136]

Table 2. The diffusion coefficient of rods and its longitudinal and transverse components for different reduced densities.[135]

ρ^*	D	$D_{\parallel}$	$D_{\perp}$	ρ^*	D	$D_{\parallel}$	$D_{\perp}$
1	2.40	2.59	2.30	16	0.24	0.50	0.11
2	1.16	1.37	1.05	24	0.21	0.49	0.073
4	0.61	0.82	0.51	32	0.20	0.50	0.049
6	0.44	0.60	0.36	40	0.23	0.64	0.031
8	0.34	0.53	0.25	48	0.34	0.97	0.025

In the study of translational motion, a fairly unexpected result was obtained. It was found that, in a sufficiently dense system, an increase of ρ^* entails not a decrease of D and $D_{\parallel}$, as seemingly should have been the case, but in fact their increase (Table 2). Such behaviour is associated with the fact that in a system of infinitely thin rods a change in the component of the velocity along the rod axis can occur only after a change in the rate of rotation as a result of the collision. However, for a high density and for long times, the maximum contribution to the corresponding component of the AF for the velocity $C(\mathbf{v}_1, t)$ comes only from the rods for which the rotational component of the movement is minimal. Although the fraction of such particles in the

system may be small, nevertheless they play an increasingly significant role with increase in ρ^*. Therefore, the higher the value of ρ^*, the greater the extent to which D and $D_\parallel$ are determined by particles with the maximum longitudinal velocity component.

2. The Effect of Orienting Fields

Luk'yanov et al.[137] investigated by the MD method the influence of the orienting field on flexible six-unit chains in a dense system. Each bond was acted upon by an orienting quadrupolar potential $U = -K\cos^2\gamma$, where γ is the angle between the bond vector **b** and the direction of the field. It was shown that the degree of order in the system increases with increase in K and that the order parameter η is close to unity for $K \cong 10\ kT$.

Calculations of the orientation AF for the vectors **b** indicated an anisotropy of the relaxation properties, which is manifested in the different rates of decrease of the AF components: along the field (C_γ) and in the transverse direction (C_β). It was found that the corresponding characteristic times behave differently with increased K: t_γ increases while t_β falls. This is associated with the operation of two mechanisms of the orientational mobility: (1) rapid rotational-vibrational movements of **b** in the potential well generated by the field and (2) transitions across the potential barrier separating two equilibrium positions of **b** (parallel and antiparallel to the field). For the relaxation of C_γ, transitions precisely through this barrier are necessary, their frequency decreasing with increase of K. On the other hand, the relaxation of C_β does not require that a barrier be overcome; vibrations at the bottom of the potential well are sufficient for this purpose and their frequency increases with increasing steepness of the potential.

The molecular dynamics of liquid alkanes has been studied in the field of external compressing and displacing forces.[138] Their intramolecular vibrational and rotational movements were considered and it was established that the external forces cause only a reorientation of the molecules but do not alter their distribution with respect to conformational states. The authors concluded that, in real experiments designed to study double refraction in a flow (the Maxwell dynamo-optical effect), the conformational composition of short hydrocarbon chains should not change appreciably compared with the static system in the absence of shear stresses.

The deformation of polyethylene chains stretched by pulling on the ends has been investigated by the MC method.[139] The "isoenergetic mechanism" of the increase in length, according to which the initial increase in length is due to a redistribution of the conformers in the chain and the change in the conformational composition begins only after numerous repetitions of the stretching process (~0.6), was confirmed.

3. The Rotational-Crystalline State

In a rotational crystal there is a possibility of the rotation of the molecules about their long axes, whereas the axes themselves retain an ordered arrangement. This state is characteristic of normal paraffins. Computer modelling of a rotational system has been carried out by the MD method.[140] A system comprising $C_{10}H_{22}$ molecules, in which the extreme H atoms were kept near the opposite ends of the chain (prism 1.3 nm high) by a harmonic potential, was considered. The chains bounding the cell along the x and y axes were stationary and 17 internal chains migrated in accordance with Newton's equations. The interaction of the C and H atoms was described by the atom–atom potentials. At the end of the initial relaxation period, numerical experiments

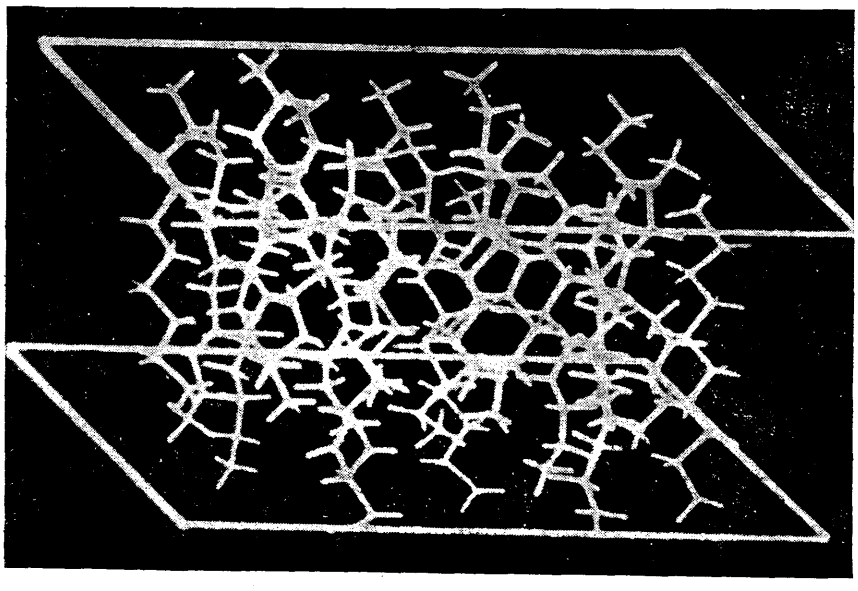


Figure 10. A film frame demonstrating the dynamics of the change in the configuration of a rotational hydrocarbon crystal.[40] The ends of the chains are held outside two opposite planes by a harmonic potential. The stationary chains bounding the cell are not shown; only the bonds between the C and H atoms are represented but not the atoms themselves.

were carried out at time intervals of ~7 ps (which corresponds to approximately three characteristic time units τ). The calculation showed that the rotational-crystalline state, in which the internal paraffin chains in the cell rotate, obtains at temperatures in the range 205–269 K. At 205 K the amplitude of the torsional vibrations of the torsional C–C angles via the equilibrium position reaches 60°, while at 269 K it reaches 120°.

Balabaev et al.[140] filmed a graphical computer display on which the configurations of a rotational crystal were shown in succession. In a literal sense, the film makes it possible to see and analyse all the details of the movements of atoms in the system (Fig.10). Visualisation of information of this kind is a powerful means for a clear description of complex molecular models in the course of a dynamic computer experiment.

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The examples of the use of the computer experiment method examined in this review by no means exhaust the numerous problems which are solved with its aid in the chemistry and physics of polymers. One may mention in addition computer studies of chemical macromolecular reactions[141] and gel formation phenomena,[142,143] the structures and mechanical properties of polymer networks,[144,145] the mechanisms of the breakdown of solid polymers,[146] crystallisation kinetics,[147] and topological effects in polymers.[148,149] The first attempts have been made to model non-equilibrium systems[150,151] and complex macromolecular objects of biological origin, for example, biological membranes.[130–132,152–157] The computer experiment frequently constitutes the only source of unique information. Vigorous studies have been initiated recently on the mathematical modelling of biopolymers: polypeptides and globular proteins in the course of their functioning[10,11,158–183] and also polynucleotides.[184–189]

Further progress in the chemistry of simulation modelling of molecular systems is probably to be expected not so much in the development of the numerical methods themselves as in the solution of strictly engineering problems in the construction of multiprocessor special purpose computers. An ideal procedure for the study of a system of N interacting particles would involve the use of a computing device having the same number of N microprocessors working in parallel, each of which would carry out calculations for only one particle. Calculations on specialised computers of this kind have already been reported in the literature.[190,191] Considerable advances have been achieved using computers with a vector processor.[192,193] Definite hopes for a qualitative improvement of the effectiveness of the numerical modelling of many systems are nowadays associated also with the prospect for the creation of a computer on the basis of the so-called reversible cellular automatic device.[194,195]

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