

THE MOLECULAR DYNAMICS OF A POLYMER CHAIN MADE UP OF INTERACTING UNITS. RELAXATION TIMES*

N. K. BALABAYEV, YU. YA. GOTLIB, A. A. DARINSKII and I. M. NEYLOV

Institute of Macromolecular Compounds, U.S.S.R. Academy of Sciences
Computer Research Centre, U.S.S.R. Academy of Sciences

(Received 5 December 1977)

The motion of a polymer chain consisting of 123 interacting units connected by rigid bonds, has been simulated on a computer, by the method of molecular dynamics. A condensed system with a high degree of filling of the volume is discussed. The equilibrium local conformation proves to be close to the conformation of the same chain in a θ solvent. The configuration of the normal coordinates for the given model is close to that of the normal modes for a linear, visco-elastic model with the same number of elements. The dependence of $\tau_{\min}/\tau(\psi)$ on wave number (ψ) ($\tau(\psi)$ represents relaxation times) is practically the same as the corresponding relationship for the visco-elastic model of Hearst and Harris, over the range of ψ corresponding to the scale of movement of two to ten units.

PHENOMENOLOGICAL, elastic models are used extensively for description of the motion of a polymer chain [1-3]. The kinetic units of these models simulate sections of the chain containing a large number of monomer units, or subchains. The interaction of these with their environment is controlled by viscous friction, and the interaction of neighbouring elements with one another, by elastic forces. Because of their nature these models are called upon for description of motion on a scale greater than the size of several statistical chain segments.

To describe motion on a smaller scale it is necessary to transfer to more detailed models in which the element would need to be not a flexible subchain, but a monomer unit or a segment containing a few monomer units, i.e. a fairly rigid kinetic unit. Approximate analytical treatment of such models is possible only in certain special cases, namely for the rotational isomer, lattice model [4-6] and for a freely articulated chain of semi-rigid elements [7]. Moreover, all the above models have a substantial disadvantage, they do not take account of intermolecular interaction between units spaced at some distance from one another along the chain. Meanwhile, allowance for the effect of these interactions on the relaxational properties of polymers is one of the central problems of the theory that have not yet been resolved. This problem becomes especially important in the case of concentrated polymeric systems (solutions and melts).

* Vysokomol. soyed. A20: No. 10, 2194-2201, 1978.

A completely correct approach requires simultaneous consideration of the rigidity of the chain elements, their interaction with one another, and with particles of the surrounding medium. The difficulties that arise in obtaining an analytical solution to such a many sided problem, are very large. The most satisfactory methods for solving these problems, are those in which molecular motion is simulated on a computer. Application of the Monte Carlo method to study of the mobility of polymer chains requires the use of lattice models of the chains, however, and introduction of simplifying, *a priori* assumptions about a discrete mechanism of motion [8, 9]. A method free from these limitations is the alternative method of simulation of molecular motion on a computer, i.e. the molecular dynamics (MD) method, which is used extensively in study of the properties of simple liquids [10, 11]. The numerical experiments used in the MD method, consist in finding the coordinates and rates of the particles after given intervals of time. For this, equations of motion of all the particles of the system are solved on the computer. A variant of this method for description of the motion of an isolated polymer chain with rigid bonds, was first worked out in [12]. Reaction of the bonds was taken into account by the Lagrange factor method [13]. An algorithm has been proposed for simulation of a chain in a liquid [4]. As a result of the methods developed in these papers, it become possible to set up numerical experiments for systematic study of molecular motion in polymeric systems. In the work presented in the present paper the molecular motion of a polymer chain consisting of interacting particles, joined by rigid bonds, is simulated. The motion of a chain in a condensed polymer system is discussed.

For viscoelastic models of a polymer chain [1-3] there is a spectrum of normal modes (types of motion) and of characteristic relaxation times corresponding to these. The normal modes of these models are certain linear combinations $\mathbf{M}(\psi)$ of the coordinates of elements of the chain x_j

$$\mathbf{M}(\psi) = \sum_{j=1}^N (x_{j+1} - x_j) \sin j\psi = \sum_{j=1}^N u_j \sin j\psi, \quad (1)$$

where x_j is a coordinate of the j th particle of the chain, $u_j = x_{j+1} - x_j$ is the projection of the j th unit of the chain, joining the $(j+1)$ th and the j th particles, $\psi = k\pi/(N+1)$ is the wave number for the k th normal mode (or the phase shift between the displacements of the projections of neighbouring chain units), N is the number of chain units and $N+1$ the number of particles.

The autocorrelation functions of these normal modes

$$\rho(\psi, t) = \langle \mathbf{M}(\psi, 0) \mathbf{M}(\psi, t) \rangle \quad (2)$$

($\langle \rangle$ denotes averaging with respect to the random ensemble) decrease exponentially with the characteristic relaxation times $\tau(\psi)$

$$\rho(\psi, t) = \rho(\psi, 0) \exp\left(-\frac{t}{\tau(\psi)}\right) \quad (3)$$

The dependence of $\tau(\psi)$ on the wave number ψ has, for the simplest models, the Kargin-Slonimskii-Rouse form

$$\tau(\psi) = \frac{\tau_0}{1 - \cos \psi}, \quad (4)$$

where $\tau_0 = \zeta l^2 / 6kT$, ζ is the coefficient of friction; l , the mean square length of the subchain; k , the Boltzmann constant and T the absolute temperature. In

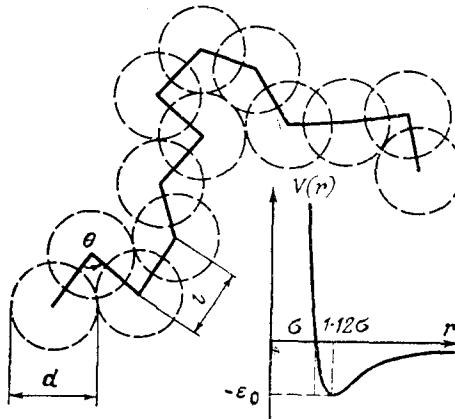


FIG. 1. Model of a chain and the interaction potential between the particles of the chain. The diameter of the particles, $d = 1.12\sigma$, corresponds to the minimal interaction potential.

the case of the Hearst-Harris chain models [3], where additional elastic interaction is introduced, resulting in the appearance of rigidity of the chain against flexure

$$\tau(\psi) = \frac{\tau_0}{1 - \cos \psi} \frac{1 - \cos^2 \theta}{1 + 2 \cos \theta \cos \psi + \cos^2 \theta}, \quad (5)$$

where $\cos \theta$ is the cosine of the "valence" angle between neighbouring sub-chains.

In the present work the following tasks were set: 1) to discover whether the exponential relationship (3) for the normal modes (linear combinations (1)), applies also to the model of rigid, interacting units discussed here; 2) to find the characteristic relaxation times for this model and to compare their dependence on ψ with the corresponding relationship for visco-elastic models.

Model and method of calculation. All the numerical calculations were made on a chain model consisting of 123 particles, joined by rigid bonds of length l , interacting with one another with a Lennard-Jones potential (Fig. 1) of

$$U(r) = 4\epsilon_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (6)$$

where σ and ϵ_0 are parameters of the Lennard-Jones potential, having the dimensions of

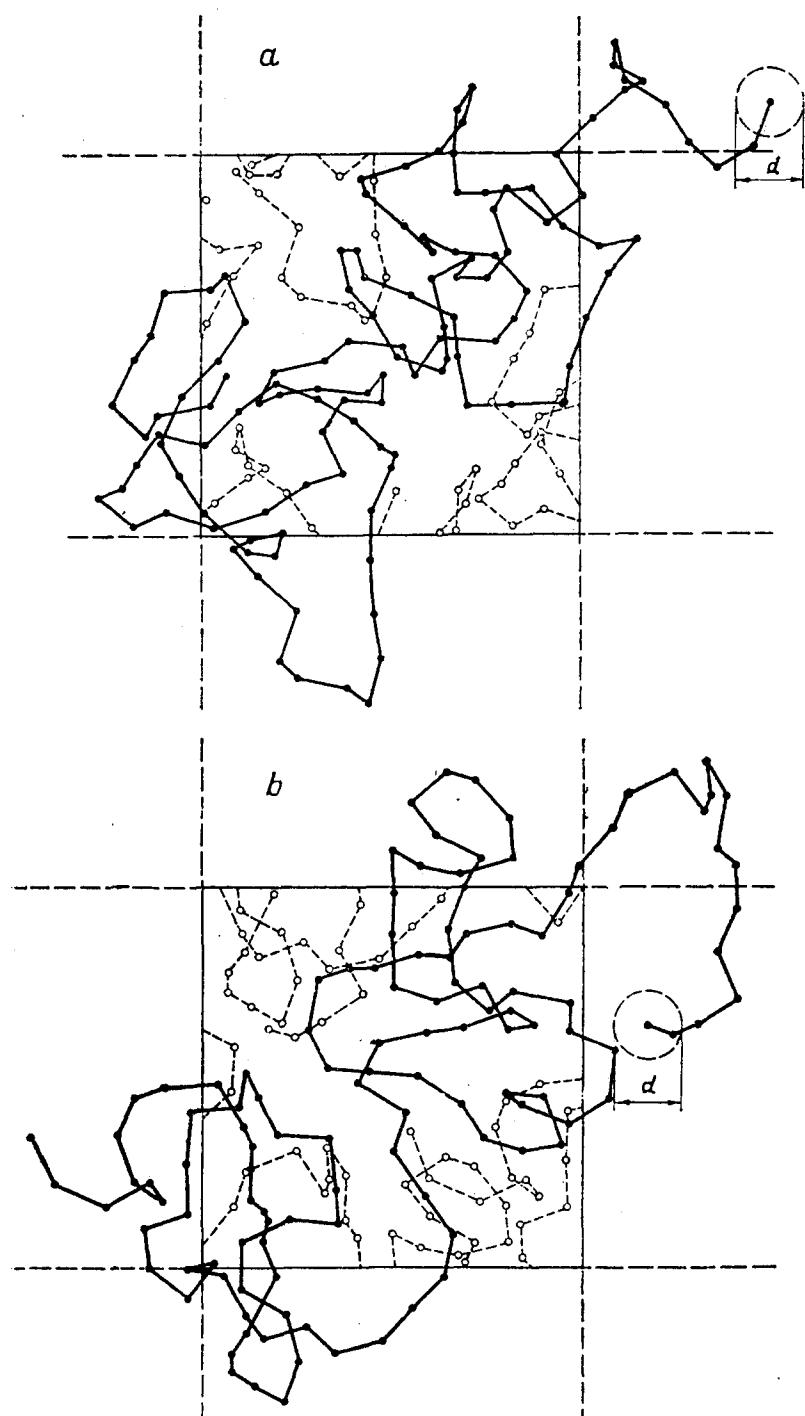


FIG. 2

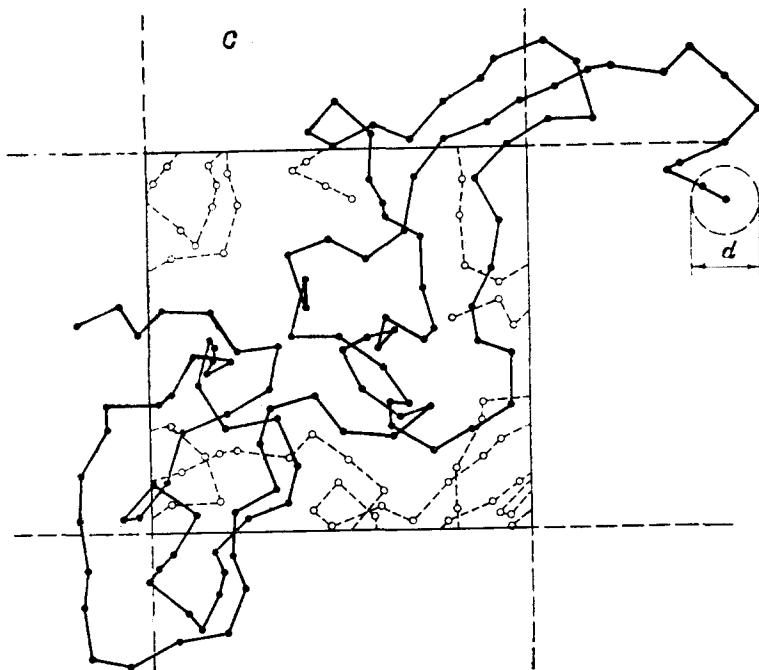


FIG. 2. Three consecutive chain configurations (*a-c*) at intervals of 6000 calculation steps (projections on the *XY* plane). Projections of the "actual" coordinates of the chain units are shown by continuous lines, and periodic continuations of these by dotted lines. The centres of particles interacting with one another with a Lennard-Jones potential, are indicated by dots. For one of the particles its "diameter", $d=1.12\sigma$, corresponding to the potential minimum, is shown.

length and energy respectively, and r is the distance between the centres of interaction. When $r=\sigma$, $U=0$ and when $r=1.12\sigma$ U has a minimal value of $+\epsilon_0$.

The occurrence of interaction between the j th and $(j+2)$ th particles limits the change in the "valence" angle between contiguous bonds, depending on the ratio of l to σ . In the given numerical experiments l was chosen such that the minimal potential energy of interaction between the j th and $(j+2)$ th particles corresponded to the tetrahedral angle between the $(j+1)$ th $(j+2)$ th bonds. The characteristic space scale of the problem is σ , and the time scale $\tau_0=\sigma\sqrt{m/\epsilon_0}$, where m is the mass of the polymer or solvent particle. All linear measurements are expressed in units of σ . The algorithm for solution of the set of equations of motion is similar to the one described in [12], but in contrast to [12] periodic boundary conditions are applied, which enable a high degree of filling of the volume of the unit cell (dimensions $5 \times 5 \times 5$) by chain units to be achieved. In addition to the chain, four "solvent" particles equivalent to the particles of the macromolecule, were introduced for the purpose of studying the diffusion of small molecules in a polymeric matrix. If each particle is described by the volume of a sphere of diameter 1.12σ , the total volume occupied by all the particles in the cell (taking into account overlapping of neighbouring particles of the chain) in the given systems, is the fraction 0.66 of the total volume of the cell. Then the degree of filling, i.e. the ratio of the occupied volume to the volume that would be occupied by unlinked particles at the maximal packing density, is 0.89.

The total energy E of the system is fixed and must be maintained during the calculation. The degree of preservation of E is used for monitoring the accuracy of integration of the

equations of motion. The calculation step $t_{\text{calc}}=0.004 \tau_0$, chosen in these experiments, led to deviation of E from the set value of not more than 1%. The temperature of the system T^* (measured in units of $T=\varepsilon_0/k$) was specified by the mean kinetic energy. Three series of numerical experiments were carried out at $T_1^*=1.58$, $T_2^*=2.03$ and $T_3^*=3.30$. At the beginning of each experiment a configuration chosen at random was set up and this was then evolved in accordance with the equations of motion. (A more detailed account of the setting up of the initial conditions is given in reference [12]). Several experiments were run at each temperature for different initial configurations. Each numerical experiment consisted of 13,000 steps and took up about 2 hr of machine time on a BESM-6 computer.

Figure 2 presents projections of the coordinates of the chain units on a plane, for three configurations corresponding to three different moments of time (after 6000 steps). This kind of instantaneous illustration of the conformation of a chain enables the nature of the motion in a polymer coil to be represented graphically. It is seen for example that the vector \mathbf{h} (the distance between the ends of the chain) changes little during the time of the experiment, whereas the vector \mathbf{r}_{60-63} , joining nearby units, is much more variable. Note that the shape of the coil is anisotropic. The orientation of the coil as a whole changes only slightly during the experiment.

In the course of these experiments the following quantities were obtained, averaged over the total time of calculation t_{tot} :

1) the mean square distances $\langle r_{jk}^2 \rangle_{\text{tot}}$ between the j th and k th particles in the chain, for certain values of j and k ;

2) the instantaneous autocorrelation functions (1)

$$\rho(\psi, t) = \frac{1}{t_{\text{tot}}} \int_0^{t_{\text{tot}}} \mathbf{M}(\psi, S) \mathbf{M}(\psi, S+t) dS \quad (7)$$

To obtain sufficiently representative averages the maximal interval in calculation of the correlators of (7), $0 < t < t_{\text{cor}}$, was selected to give $t_{\text{cor}}=t_{\text{tot}}/30$. For fairly rapidly relaxing (in comparison with t_{tot}) quantities, averaging of (7) with respect to the time t_{tot} , differs little from averaging with respect to a random ensemble.

The quantities $\langle r_{jk}^2 \rangle$ were used to obtain information about the local, conformational microstructure of the chain. The autocorrelation functions for r_{jk}^2 when $|j-k| \leq 7$ fell rapidly during the time of calculation of the correlator t_{cor} , and hence it may be said that equilibrium values of $\langle r_{jk}^2 \rangle$ are established at $|j-k| \leq 7$. Figure 3 shows curves of the dependence of $\langle r_p^2 \rangle$ on $p=|j-k|$, obtained at three temperatures. It is seen that the $\langle r_p^2 \rangle=f(p)$ relationship becomes linear after $p=2$. On the same graph we include theoretical curves of the $\langle r_p^2 \rangle=f(p)$ relationship for model chains with free internal rotation and with different values of the mean cosine of the angle between contiguous units, $\cos \alpha$, where $\alpha=\pi-\theta$ is the angle additional to the "valence" angle θ

$$\frac{\langle r_p^2 \rangle}{l^2} = p \frac{1+\cos \alpha}{1-\cos \alpha} - \frac{2\cos \alpha}{(1-\cos \alpha)^2} (1-\cos^p \alpha) \quad (8)$$

For the given temperatures T^* , from 1.58 to 3.30, the experimental points lie on the theoretical curves with $\cos \alpha \approx 1/2$ ("valence" angle $\theta=120 \pm 5^\circ$). Direct calculation of $\cos \alpha$ for the angle between contiguous bonds, allowing for interaction of only the j th and $(j+2)$ th particles, also gives $\cos \alpha=1/2$ ($\theta=120^\circ$).

Consequently the local conformational properties of the given model of a polymer chain, even with such close packing of the units, are similar to the conformational properties of a separate chain with free rotation, in solution (in a θ solvent).

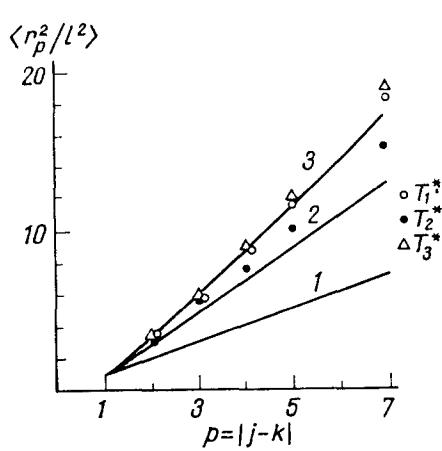


FIG. 3

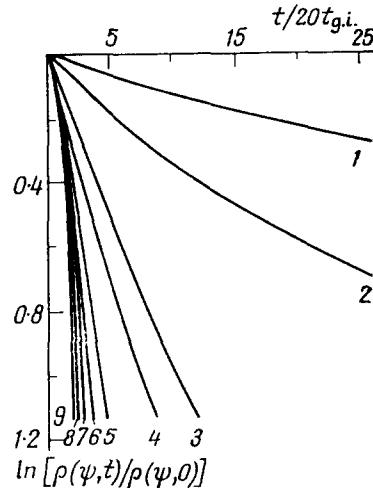


FIG. 4

FIG. 3. Dependence of the mean square distance $\langle r_p^2 \rangle$ between the ends of chain segments comprising p -particles ($p-1$ units), on p at $T_1^*=1.58$, $T_2^*=2.03$ and $T_3^*=3.30$. The continuous lines show the dependence on p for a freely articulated chain (1), a chain with the tetrahedral valence angle (2) and a chain with a valence angle of 120° (3).

FIG. 4. Dependence of $\ln [\rho(\psi, t)/\rho(\psi, 0)]$ for the instantaneous correlation functions $\rho(\psi, t)$ at $\psi=k\pi/10$. The numbers on the curves correspond to $k=1, 2, \dots, 9$ (the number of the normal mode), $N=123$.

Time relationships, $\ln \rho(\psi, t)$, for a number of values of ψ , corresponding to the high frequency part of the relaxation spectrum (from $\psi=\pi$ to $\psi=\pi/10$), are shown in Fig. 4. Strictly speaking, for a finite chain the minimal model corresponds to the wave number $\psi_{\min}=122\pi/123$. We examined the case where $\psi=\pi$, for which, instead of expression (1) the correlation function for

$$M(\pi)=\sum_{j=1}^N (-1)^j u_j \quad (9)$$

must be taken.

Since there is little difference between ψ_{\min} and π , the error introduced by this substitution is small. Variation in ψ from π to $\pi/10$ corresponds to a change in the length of the "wave" $\Lambda=2\pi/\psi$ of the corresponding normal mode, i.e. in a quantity characterizing the scale of movement from $\Lambda=2l$ to $\Lambda=20l$. The change in the quantity $\rho(\psi, t)$ for the slowest, largest scale motions ($\psi=\pi/10$) examined, is small in the time t_{cor} , and this prevents reliable determination of the quantitative characteristics of the corresponding movements. In the range $\pi/5 \leq \psi \leq \pi$ the time relationships $\ln \rho(\psi, t)$ are linear, at least as far as a fall in

$\rho(\psi, t)$ by a factor e in comparison with the initial value $\rho(\psi, 0)$. It follows from this that the linear combinations $M(\psi)$, in accordance with expression (3) are close to the normal modes for the given chain model. The relaxation times $\tau(\psi)$ were found from the slopes of the $\ln \rho(\psi, t) = f(t)$ curves. The $\tau_{\min}/\tau(\psi)$ curves constructed in Fig. 5 are monotonic. The smallest scale mode ($\psi_{\min} = \pi$) corresponds to the minimal time $\tau_{\min} = \tau(\pi)$. The results of the numerical experiments were compared with the corresponding $\tau_{\min}/\tau(\pi)$ curves for the Kargin-Slonimskii-Rouse model (1), and for the Hearst-Harris model (2) with $\cos \alpha = 1/3$. The experimental points lie mainly between these two curves, moving toward curve (2) with reduction in temperature.

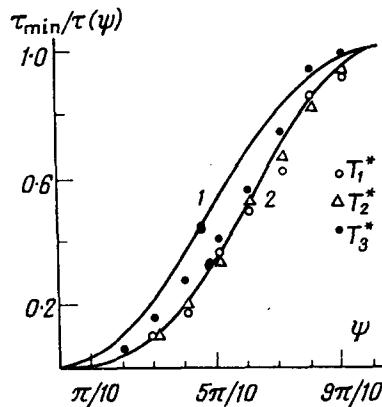


FIG. 5. Dependence of the ratio of relaxation times $\tau_{\min}/\tau(\psi)$ on wave number ψ at $T_1^* = 1.58$, $T_2^* = 2.03$ and $T_3^* = 3.30$. The continuous lines are the curves for the subchain model (1) and the Hearst-Harris model with $\cos \alpha = 1/3$ (2).

It follows from the above data that the equilibrium, local conformation (the value of $\langle r_p^2 \rangle$) of a polymer chain in a close-packed polymeric medium is practically the same as the conformation of the same chain in a θ -solvent. The cosine of the average angle between contiguous units, $\cos \alpha$, is dependent only on the interaction between these contiguous units in the given chain. This is applicable to values of $\langle r_p^2 \rangle$ that are in accord with accepted ideas about the structure of macromolecules of amorphous polymers in bulk [15–18]. In contrast to reference [18], in this work we use a polymer chain model without a lattice, having realistic potential energies of interaction and with a “valence” angle. In the model discussed the units interact with one another with non-linear Lennard-Jones potentials. The reaction of the bonds are also complex, non-linear functions of the coordinates and rates of motion of the chain elements. Nevertheless, linear combinations of chain coordinates exist, which in the given model relax according to the simple exponential law (3), with a single relaxation time. The form of these normal modes (the coefficients of the linear combinations) is close to that of the normal modes for the Kargin-Slonimskii-Rouse, linear

visco-elastic model [1, 2], i.e. for a chain consisting of spheres, as centres of viscous resistance, and springs. The $\tau_{\min}/\tau(\psi)$ (or $\tau_{\min}/\tau(\Lambda(\psi))$) relationship in the range $\Lambda(\psi) = (2-10)l$ is close to the corresponding relationship for visco-elastic models and is practically the same as $\tau_{\min}/\tau(\psi)$ for the Hearst-Harris model [3], with $\cos \alpha = 1/3$ (which corresponds to the tetrahedral angle between the units). A not unimportant result here is the fact that despite steric hindrance arising as a result of powerful interaction of units some distance apart along the chain but connected in series, the $\tau_{\min}/\tau(\psi)$ relationship is determined by their linear connections in the chain, and does not differ from the relationships for linear, visco-elastic models. It is important to note that the form of the $\tau_{\min}/\tau(\psi)$ relationship for visco-elastic models is maintained down to normal modes of smallest scale; of size comparable with that of a long, rigid band. It follows from the results of numerical experiments that the form of the $\tau_{\min}/\tau(\psi)$ relationship is only slightly sensitive to temperature for the values of $kT > \varepsilon_0$ examined (a system of the type of a molten polymer).

It is well known that in real chains there are barriers to internal rotation. The height of these barriers, even in kinetically and thermodynamically flexible chains (PE) can be several kilocalories per mole, and hence are higher than kT at the usual experimental temperatures. In the case of such chains the kinetic units and statistical segments comprise several units. The authors consider that the chain model studied in the present paper can describe the motion of such kinetic units in real chains and take into account their inherent volume and interaction between the units. In this sense the proposed model can be used for description of segmental motion in polymers in the high elastic state or in the melt, at least for local, small scale forms of motion (the smallest distances between entanglements, for example). The results of the numerical experiments show that with respect to local conformational properties and local movements, the model behaves like visco-elastic models with a kinetic unit and statistical segment of similar magnitude to the unit of our model. By means of this model it is possible to examine the movement of real chains in which the lengths of the statistical segment and kinetic unit are commensurate.

The results of this work provide a theoretical basis for application of dynamic, viscoelastic models to description of the relaxational properties of polymers in the high elastic state and in the melt (see for example [1] and [19]).

Translated by E. O. PHILLIPS

REFERENCES

1. V. A. KARGIN and G. L. SLONIMSKII, Kratkie ocherki po fiziko-khimii polimerov (Short Essays on the Physical Chemistry of Polymers). Izd. "Khimiya", 1967
2. P. E. ROUSE, J. Chem. Phys. **21**: 1272, 1953
3. R. A. HARRIS and J. E. HEARST, J. Chem. Phys. **44**: 2595, 1966
4. Yu. Ya. GOTLIB and A. A. DARINSKII, Sb. Relaksatsionnye yavleniya v polimerakh (Collected papers. Relaxation Effects in Polymers). p. 283, Izd. "Khimiya", 1972

5. Yu. Ya. GOTLIB and A. A. DARINSKII, Vysokomol. soyed. A11: 2400, 1969 (Translated in Polymer Sci. U.S.S.R. 11: 11, 2725, 1969)
6. K. IWATA, J. Chem. Phys. 54: 12, 1971
7. Yu. Ya. GOTLIB, Sb. Relaksatsionnye yavleniya v polimerakh (Collected papers. Relaxation Effects in Polymers). p. 263, Izd. "Khimiya", 1972
8. P. H. VERIER and W. H. STOCKMAYER, J. Chem. Phys. 36: 227, 1963
9. Yu. A. TARAN, Vysokomol. soyed. A13: 2020, 1971 (Translated in Polymer Sci. U.S.S.R. 13: 9, 2272, 1971)
10. B. ALDER and T. WAINWRIGHT, J. Chem. Phys. 27: 1208, 1957
11. A. RAHMAN, Phys. Rev. A405: 136, 1964
12. N. K. BALABAYEV, A. G. GRIVTSOV and E. E. SHNOL', Chislennye eksperimenty po modelirovaniyu dvizheniya molekul (Numerical Experiments on Simulation of Molecular Motion). Part III, Preprint No. 4, IPM, U.S.S.R. Academy of Sciences, Moscow, 1972
13. N. N. BUKHGOL'TS, Osnovnoi kurs teoreticheskoi mekhaniki (Basic Course of Theoretical Mechanics). Part 2, Izd. "Nauka", 1966
14. N. K. BALABAYEV, A. G. GRIVTSOV and E. E. SHNOL', Dokl. Akad. Nauk SSSR 220: 1096, 1975
15. P. J. FLORY, Principles of Polymer Chemistry, Ithaca, New York, 1953
16. J. E. COTTON, D. DECKER, H. BENOIT, B. FURNOUX, J. S. HIGGINS, G. JANNINK, R. OBER, G. PICOT and J. CLOIZ, Macromolecules 7: 863, 1964
17. G. D. WIGNALL, J. SCHELTEN and D. G. BALLARD, J. Appl. Crystallogr. 7: 190, 1974
18. A. M. SKVORTSOV, A. A. SARIBAN and T. M. BIRSHTEIN, Vysokomol. soyed. A19: 1014, 1977 (Translated in Polymer Sci. U.S.S.R. 19: 5, 1169, 1977)
19. J. D. FERRY, Vyazkouprugie svoistva polimerov (The Visco-elastic Properties of Polymers). Foreign Literature Publishing House, 1963 (Russian translation)