A STATISTICAL MODEL OF LINEAR POLYMERS IN THE AMORPHOUS STATE

Yu. A. Buevich

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A statistical theory of polymer-solvent systems has been developed on the basis of a simple lattice model assuming wholly random packing of the linear chain molecules in the lattice. It is assumed that the entire system is placed in simple tension or compression. The applications of the model are discussed in relation to the construction of theories of polymer solutions, true and forced high elasticity, and phase transformations in polymer systems. As distinct from existing theories, the proposed model accounts for a number of important observable effects; the change in volume associated with the dissolving or diluting of a polymer, negative entropies and heats of mixing, deviations from the classical theory of high-elastic deformation, etc.

The principal difficulty in constructing a physical theory of polymers consists in the computation of the partition function and the corresponding thermodynamic functions, especially in cases in which the polymer is subjected to external influences. The development of statistical methods are applied to polymer systems (in particular, methods based on the use of various lattice models) was begun by Flory and Huggins (see, for example, the review in [1]). Later, these methods were considerably improved [2, 3]. Our object here is a generalization of the theory that will make it possible to evaluate in explicit form the effect of the free volume of the system and especially the stresses in the polymer material (and hence the associated anisotropy) on its equilibrium states. For the sake of simplicity we consider only a simple variant of the theory, in which the quality of the investigated phenomena is preserved, while details characteristic of individual specific polymers are neglected. The theory can be further refined with the object of more closely approximating actual situations by discarding certain of the initial assumptions; as a rule, these refinements are obvious. The theory can be extended to branched polymers by means of the results of [2, 3]. In what follows neither of these two points receives special mention.

§1. MODEL AND COMPUTATION OF STATISTICAL SUM

As our model of the polymer-solvent system we employ a lattice with $n = n_0 + n_s + mn_p$ cells and coordination number z,* occupied by n_s solvent molecules, n_p polymer molecules containing m monomer units (segments) each, and n_0 vacancies (holes). Thus, the volumes of the polymer segments and the solvent molecule are assumed to be the same and equal to the cell volume, which, however, may depend on temperature and pressure.

Let the number of bonds between neighboring segments of the j-th polymer molecule oriented in the i-th direction ("bonds of type i") be $m'^{(j)}_i$; obviously, $\Sigma_i m'^{(j)}_i \equiv m-1$.

We call a sequence of two bonds of type i, i. e., i → i, a trans isomer of type i, and a sequence i → i', i' ≠ i a "folded" isomer of type i, where i is an arbitrary number from the set 1, 2, ..., z.

If the number of isomers of type i in the j-th molecule of the polymer is $m_i^{(j)}$, then $\Sigma_i m_i^{(j)} \equiv m-2$; if the fraction of folded isomers of type i in this molecule is $f_i^{(j)}$ $(0 \leqslant f_i^{(j)} \leqslant 1)$, then $\Sigma_i f_i^{(j)} m_i^{(j)} = f^{(j)}(m-2)$, where $f^{(j)}$ is the fraction of folded isomers of any type in the molecule.

We assume that the trans isomers may occupy one of N torsional vibration levels with energies ε_k (k = 1, ...

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*The coordination number z of the lattice is the total number of bonds possible between a certain element (for example, a segment) and the elements in neighboring cells of the network; generally speaking, $z \geq z'$, where z' is the number of possible bond directions between neighboring segments of the chain molecules (number of permissible isomers), so that a lattice with coordination number z' is, as it were, embedded in a lattice with coordination number z (see [2]). Below, for simplicity, we assume that $z = z'$; the extension to the arbitrary case $z \neq z$ involves the simultaneous consideration of both lattices and does not present difficulties.

..., N'), and the folded isomers one of N' levels with energies $\varepsilon_k' + \Delta\varepsilon$ (k = 1, ..., N'), where $\Delta\varepsilon$ is the energy difference between the lower vibrational levels for the folded and trans isomers.

We assume that the entire system is located in a simple tension (or compression) field, so that a tensile force τ acts on each chain molecule; we orient the lattice so that one of its principal axes coincides with the direction of action of τ.

We note that these assumptions are quite usual in polymer statistical physics and do not affect the qualitative characteristics of the phenomena discussed below. Where necessary they can be discarded, the desirability of this step being determined separately in each specific case. For example, the Flory-Huggins theory of polymer solutions completely disregards the volume change associated with mixing. In section 3 this effect is described in terms of a corresponding change in the number of holes, i.e., the free volume. It may be expected, however, that differences in the length of the covalent intramolecular bonds and hydrogen or van der Waals intermolecular bonds also make a certain contribution to this effect. If the object were to describe the effect of these differences, it would be natural to start by discarding the constraints imposed on the volumes of the lattice elements.

After computations, we write the following relation for the number of possible states of the system:

$$W = W_1 W_2 W_3 W_4 W_5$$

$$W_1 = \left(\frac{1}{2n^{m-1}}\right)^{n_p} \frac{n!}{n_p!\,(n_s+n_0)!}, \quad W_2 = \prod_{j=1}^{n_p} \prod_{i=1}^{z} \frac{m_i^{(j)}!}{(f_i^{(j)} m_i^{(j)})!\,((1-f_i^{(j)})\, m_i^{(j)})!}$$

$$W_3 = \prod_{j=1}^{n_p} \left(\frac{z-2}{z}\right)^{f^{(j)}(m-2)} (f^{(j)}(m-1))! \prod_{i=1}^{z} \frac{1}{(f_i^{(j)} m_i^{\prime(j)})!}$$

$$W_4 = \frac{(n_s+n_0)!}{n_s!\,n_0!}, \quad W_5 = \prod_{j=1}^{n_p} \prod_{i=1}^{z} (f_i^{(j)} m_i^{(j)})!\,((1-f_i^{(j)})\, m_i^{(j)})! \times$$

$$\times \left(\prod_{k=1}^{N'} \frac{1}{(c_{ik}^{\prime(j)} f_i^{(j)} m_i^{(j)})!}\right) \left(\prod_{k=1}^{N} \frac{1}{(c_{ik}^{(j)} (1-f_i^{(j)})\, m_i^{(j)})!}\right), \quad \sum_{k=1}^{N} c_{ik}^{(j)} \equiv \sum_{k=1}^{N'} c_{ik}^{\prime(j)} \equiv 1 \qquad (1.1)$$

Here, $c_{ik}^{(j)}$ and $c_{ik}^{\prime(j)}$ are the fractions of trans and folded isomers of type i in the j-th polymer molecule at the k-th vibrational level. The first factor in (1.1) describes the number of packings of the n_p polymer molecules in the lattice on the assumption that the sequence and type of bonds are fixed in each molecule, the second factor describes the increase in the number of packings associated with the mixing of trans and folded isomers, while the third factor describes the corresponding increase associated with the possibility of isomer type changes.

The fourth factor in (1.1) is the number of indistinguishable arrangements of the n_s solvent molecules in $n_s + n_0$ cells and, finally, the fifth factor describes the degeneracy of the states with a given packing owing to the presence of a large number of torsional vibration levels. When explicit expressions are substituted for W_i from (1.1) in the product for W, the latter is somewhat simplified. The form of (1.1) is convenient, however, in the sense that it makes it possible to distinguish in the expressions for the various thermodynamic functions terms associated with factors of different physical origin.

The quantity W can be calculated from (1.1) as follows. We consider the progressive occupation of the lattice by polymer molecules with a fixed bond sequence. Assume that j molecules have already been introduced into the lattice; then the first segment of the (j + 1)-th molecule can be placed in n − jm ways. The conformation of the molecules is assumed given; therefore, any subsequent (k + 1)-th segment of the (j + 1)-th molecule can occupy, if the position of the initial segment is fixed, only one, perfectly definite cell. The probability a_{jk} that this cell is free can be estimated as the "surface" fraction of free cells introduced by Huggins, or less accurately, but more simply, as the "volume" fraction of such cells introduced by Flory. The corresponding expressions for a_{jk} have the form:

$$a_{jk} = \frac{z(n-mj-k)}{z(n-mj-k) + [(z-2)\,m+2]\,j + (z-2)\,k + 2}, \quad a_{jk} = \frac{n-mj-k}{n} \qquad (1.2)$$

A more accurate calculation, in which the nonequivalence of orientation of the (k + 1)-th segment in different directions from the k-th segment is taken into account, can be based on the results presented in [3]. In what follows, for simplicity, we employ the second of expressions (1.2); the quantitative difference between calculations based on the different expressions for a_{jk} is usually very small. As a result for the number of arrangements of the (j + 1)-th molecule with fixed bonds we have the expression

$$w_1^{(j+1)} = (n - mj) \prod_{k=1}^{m-1} a_{jk} = \frac{1}{n^{m-1}} \frac{(n - mj)!}{(n - m(j+1))!}$$

Multiplying the numbers $w_1^{(j)}$ for all the molecules and then multiplying the product by the Boltzmann factor $(n_p!)^{-1}$, which takes into account the indistinguishability of the polymer molecules, and the factor 2^{-n_p}, which takes into account the indistinguishability of the two end segments of each molecule, we arrive at expression (1.1) for W_1.

The number of ways of selecting $f_i^{(j)} m_i^{(j)}$ folded isomers from the total number $m_i^{(j)}$ of isomers of type i in the j-th molecule is equal to the number of combinations of $m_i^{(j)}$ elements taken $f_i^{(j)}\ m_i^{(j)}$ at a time. Obviously, the number of selections $f^{(j)}(m-2)$ of folded isomers of arbitrary type in the j-th molecule is equal to the product of the latter numbers with respect to i. By additionally multiplying them with respect to j, i.e., over all n_p molecules, we obtain the expression W_2.

In order to take into account the randomness of the distribution of types of folded or trans isomers along the polymer molecules, it is necessary to calculate the number of ways of selecting $f_i^{(j)} m_i'^{(j)}$ bonds of type i in the j-th molecule entering into the composition of folded isomers of this type from the total number $f^{(j)}(m-1)$ of such bonds of arbitrary type (in the calculation it is necessary to employ the numbers $m_i'^{(j)}$, and not $m_i^{(j)}$, as may easily be seen by forming a ring from the chain molecule by joining the first and last segments). If any sequences of heterogeneous isomers are allowed, the number of such selections for the j-th molecule will be

$$w_3'^{(j)} = C_{f^{(j)}(m-1)}^{f_1^{(j)} m_1'^{(j)}} C_{f^{(j)}(m-1)-f_1^{(j)} m_1'^{(j)}}^{f_2^{(j)} m_2'^{(j)}} \cdots C_{f^{(j)}(m-1)-\cdots-f_{z-2}^{(j)} m_{z-2}'^{(j)}}^{f_{z-1}^{(j)} m_{z-1}'^{(j)}} =$$

$$= (f^{(j)}(m-1))! \left(\prod_{i=1}^{z} (f_i^{(j)} m_i'^{(j)})! \right)^{-1}$$

In reality, for example, a trans isomer i → i may be followed by folded isomers not of z, but only of z − 2 different types. In fact, the folded isomers i → i and i → i', i' = −i are forbidden. Therefore the expression for $w_3'^{(j)}$ should be multiplied by the quantity

$$((z-2)/z)^{f^{(j)}(m-2)}$$

If, moreover, we multiply the results for the different polymer molecules, we arrive at a relation for W_3.

Finally, W_4 and W_5 are calculated in exactly the same way as W_2, if one takes into account the indistinguishability of the solvent molecules, the holes, and also the different isomers in the j-th molecule at the same vibration levels.

In an isotropic system, when $f_i^{(j)} \approx f^{(j)}$, $m_i^{(j)} \approx m^{(j)}$, etc., expressions (1.1) are considerably simplified. If we neglect vibrational degrees of freedom and the presence of a solvent and also treat the polymer molecules as cooperative systems ($f^{(j)} \approx f$, etc.), then, using for the factorials the approximation $x_p! \approx x^x$, we arrive at Flory's expression for the number of states [4]

$$W \approx \left(\frac{z(z-2)^{f(m-2)}}{2n^{m-1}} \right)^{n_p} \frac{n!}{n_p!\, n_s!} \frac{((m-2)n_p)!}{(f(m-2)n_p)!\,((1-f)(m-2)n_p)!}$$

When torsional vibrations are taken into account, we obtain the modification of this expression proposed by Vol'kenshtein [5].

Let us now consider the energy of a state with fixed parameters $n_0, f_i^{(j)}, m_i^{(j)}$, etc. In calculating the intermolecular interactions we employ the "nearest neighbor" approximations. Then the energies of the hole-segment, hole-solvent molecule, and hole-hole interactions are identically equal to zero, and for the segment-segment, solvent molecule-solvent molecule and segment-solvent molecule interactions we use the notations ε_{pp}, ε_{ss}, and ε_{ps}, respectively. In the Guggenheim approximation [6] for the total energy of the intermolecular interactions in the system we obtain

$$E_1' = -{}^1/_2 \{\varepsilon_{pp} [(z-2)m + 2]\, n_p S_p + \varepsilon_{ss} z n_s S_s + 2\varepsilon_{ps} z n_s S_p\}$$

$$S_p = \frac{[(z-2)m+2]\, n_p}{[(z-2)m+2]\, n_p + z(n_s+n_0)}, \quad S_s = \frac{z n_s}{[(z-2)m+2]\, n_p + z(n_s+n_0)} \tag{1.3}$$

Here, as the reference point for the energy E_1' we have taken the energy of the system with "disconnected" interactions (the completely dissociated system). It is convenient to take as the reference point the energy of the intermolecular interactions of the crystalline polymer and the pure solvent without holes. Then

$$E_1 = (^1/_2\ \varepsilon_{pp} + {^1/_2}\ \varepsilon_{ss} - \varepsilon_{ps})\ zn_sS_p + {^1/_2}\ zn_0\,(\varepsilon_{pp}S_p + \varepsilon_{ss}S_s) \tag{1.4}$$

We note that the Huggins approximation [7]

$$E_1 = \frac{kT\chi}{A}\frac{mn_pn_s}{mn_p + n_s}, \quad \frac{kT\chi}{A} = z\left(\frac{1}{2}\,\varepsilon_{pp} + \frac{1}{2}\,\varepsilon_{ss} - \varepsilon_{ps}\right) \tag{1.5}$$

is frequently employed.

Here, χ is the Huggins constant, which can be expressed in terms of the specific energies of evaporation or cohesion of the system components, k is Boltzmann's constant, and A is Avogadro's number. Expression (1.5) corresponds to the model of a system without holes, when it coincides with (1.4). In the presence of a large free volume relation (1.5) becomes meaningless.

The potential energy of the polymer molecules in the field of a tensile force τ is equal (the energy is reckoned from the energy of a molecule extended in the direction of action of the load [5, 8]) to

$$E_2 = \tau h \sum_{j=1}^{n_p} \sum_{i=1}^{z} m_i'^{(j)}(1 - \cos\theta_i), \quad \tau > 0 \tag{1.6}$$

Here θ_i is the angle between the direction of the force τ and the i-th bond; h is the effective bond length. In investigating the effect of compression it is insufficient simply to change the sign of τ. In fact, this corresponds merely to reflection of the system about a plane perpendicular to τ, i.e., to another possible choice of direction on the axis of extension. Accordingly, we consider compression separately; taking as zero the energy of a molecule oriented entirely in the indicated plane, we obtain an expression, analogous to (1.6), for the potential energy of the system

$$E_2 = \tau h \sum_{j=1}^{n_p} \sum_{i=1}^{z} m_i'^{(j)} \cos\vartheta_i, \quad \tau > 0, \quad \vartheta_i = \frac{\pi}{2} - |\theta_i| \tag{1.7}$$

where ϑ_i is the angle between the direction of the i-th bond and the plane.

The torsional vibration energy

$$E_3 = \sum_{j=1}^{n_p} \sum_{i=1}^{z} \left(\sum_{k=1}^{N'} c_{ik}' f_i^{(j)} m_i^{(j)} (\Delta\varepsilon + \varepsilon_k') + \sum_{k=1}^{N} c_{ik}^{(j)} (1 - f_i^{(j)})\, m_i^{(j)} \varepsilon_k \right) \tag{1.8}$$

If we neglect vibrational degrees of freedom, i.e., assume that all the isomers are at the lower levels, so that $c_{i1} = c_{i1}' = 1$, $c_{ik} = c_{ik}' = 0$, $k \neq 1$, expression (1.8) reduces to the relation proposed by Flory for describing molecular chains with limited flexibility,

$$E_3 = \sum_{j=1}^{n_p} f_i'^{(j)} (m - 2)\,\Delta\varepsilon \tag{1.9}$$

In the general case we will henceforth assume that

$$\varepsilon_k = (k - 1)\ \hbar\omega, \quad \varepsilon_k' = (k - 1)\ \hbar\omega', \quad \hbar = h/2\pi$$

Here, h is Planck's constant, and ω and ω' are the frequencies of the lower harmonics of the torsional vibrations of the trans and folded isomers, respectively.*

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*For simplicity, only two types of isomers are distinguished—folded and trans isomers. In principle, it is possible to distinguish z − 2 different types of folded isomers; then, instead of $\Delta\varepsilon$, ω' a set of z − 2 such quantities will figure in the theory.

Finally, the energy of the system in an isotropic pressure field P is represented in the form (the energy of the analogous system without holes is taken as the reference point)

$$E_4 = Pn_0 v \tag{1.10}$$

where v = v(P, T) is the volume of a lattice cell.

The partition function of the system has the form**

$$Q = \sum_{W' \geqslant 1} W(n_0, f_i^{(j)}, \ldots) \exp\left(-\frac{1}{kT} E(n_0, f_i^{(j)}, \ldots)\right), \quad E = \sum_{k=1}^{4} E_k \tag{1.11}$$

Here, the summation is carried over all possible values of the parameters n_0, $f_i^{(j)}$ etc. (apart from P, n_p, and n_s, which are assumed given), compatible with the condition $W' \geq 1$, where $W' = W/W_5$ is the number of possible ways of packing the system in the lattice.

We assume that each chain molecule and the system as a whole is a cooperative system, so that the sum (1.11) can be replaced by its maximum term with $n_0 = n_{0\max}$, $f_i^{(j)} \approx f_i = f_{i\max}$, etc. Then, omitting the subscript max, for Q we have the approximate expression

$$Q \approx W(n_0, f_i, \ldots) \exp\left(-\frac{E(n_0, f_i, \ldots)}{kT}\right), \quad W'(n_0, f_i, \ldots) \geqslant 1 \tag{1.12}$$

The replacement of the sum (1.11) by relation (1.12) is possible in view of the very sharp dependence of the term under the summation sign on the parameters involved and its very sharp maximum at a certain point of parameter space, which is generally characteristic of all systems to which the methods of statistical physics are fundamentally applicable. In the limit, as the number of elements of the system tends to infinity, the legitimacy of substituting (1.12) for (1.11) is easily demonstrated; in particular, the substitution is justified, for example, in [2], and also in [9], for systems of the type considered here.

Expression (1.12) for Q is valid only at $W' \geq 1$. It is easy to see that W' is a decreasing function of temperature, so that at a sufficiently low temperature this condition is not satisfied, and expression (1.12) leads to paradoxes, for example, the entropy of the system proves to be negative. In order to formulate the partition function in the low-temperature region, we employ, as most reasonable, the hypothesis of Gibbs and Di Marzio [2, 9], according to which the temperature T_g, at which $W' \approx 1$, is regarded as the temperature of a certain second-order phase transition (according to the Ehrenfest classification) identifiable with the glass transition associated with infinitely slow (equilibrium) cooling of the amorphous polymer. At $T < T_g$ the configuration of the system is, as it were, "frozen in": the values of all the parameters are assumed constant and equal to their values at $T = T_g$. Thus, at $T < T_g$ the partition function is represented in the same form (1.12), but n_0, f_i, etc. are calculated at the temperature $T = T_g$.

§2. THERMODYNAMIC FUNCTIONS

Using the Stirling formula, for the entropy of the system, after computations, we obtain the expression

$$S = k \ln W = S_1 + S_2 + S_3 + S_4 + S_5$$

$$S_1 = -R\,[(r_s + r_0)\ln(\varphi_s + \varphi_0) + r_p(\ln \varphi_p + m - 1 + \ln 2)], \quad R = kA$$

$$S_2 = -Rr_p\left\{\sum_{i=1}^{z}\left[m_i(f_i \ln f_i + (1 - f_i)\ln(1 - f_i)) + \right.\right.$$
$$\left.\left. + \frac{1}{2}(\ln f_i + \ln(1 - f_i) + \ln m_i)\right] + \frac{1}{2}(z - 1)\ln 2\pi\right\}$$

$$S_3 = -Rr_p\left\{-\left(\sum_{i=1}^{z} f_i m_i\right)\ln\frac{z-2}{z} + \sum_{i=1}^{z}\left[f_i m_i'\left(-\ln\sum_{j=1}^{z} f_j m_j' + \ln f_i m_i'\right) + \right.\right.$$

**It is assumed that the internal state of the segments and solvent molecules does not depend either on the method of packing in the lattice or on the development of torsional vibrations. Then the internal partition functions are excluded from consideration.

$$+\frac{1}{2}\ln f_i m_i'\Big]-\frac{1}{2}\ln\sum_{i=1}^{z} f_i m_i' + \frac{z-1}{2}\ln 2\pi\Big\}$$

$$S_4 = -R\left(r_s \ln\frac{\varphi_s}{\varphi_s+\varphi_0} + r_0 \ln\frac{\varphi_0}{\varphi_s+\varphi_0}\right)$$

$$S_5 = -Rr_p \sum_{i=1}^{z}\Big\{f_i m_i \sum_{j=1}^{N'} c_{ij}' \ln c_{ij}' + (1-f_i)\, m_i \sum_{j=1}^{N} c_{ij} \ln c_{ij} +$$

$$+\frac{1}{2}\Big[\sum_{j=1}^{N'} \ln(c_{ij}' f_i m_i) + \sum_{j=1}^{N} \ln(c_{ij}(1-f_i)\, m_i) - \ln f_i m_i - \ln(1-f_i)\, m_i\Big] - \left(\frac{1}{2}(N+N')-1\right)\ln 2\pi\Big\}$$

$$\varphi_p = \frac{mn_p}{mn_p+n_s+n_0}, \quad \varphi_s = \frac{n_s}{mn_p+n_s+n_0}, \quad \varphi_0 = \frac{n_0}{mn_p+n_s+n_0} \tag{2.1}$$

Here, the terms S_i describe the contributions to the entropy due to the factors W_i in expression (1.1) for the number of states of the system; r_p, r_s, and r_0 are numbers of moles, and φ_p, φ_s and φ_0 the volume fractions of polymer, solvent, and holes in the system. For simplicity, in what follows we assume that $m_i \gg 1$; moreover, we set $N = N' = \infty$.

Then for the entropy S and the Gibbs function Φ of the system we have the asymptotic expressions

$$S \approx -R(r_s \ln\varphi_s + r_0 \ln\varphi_0 + r_p \ln\varphi_p) - Rr_p\Big\{m - y\ln y + \sum_{i=1}^{z} m_i \Big[f_i \ln f_i +$$

$$+(1-f_i)\ln(1-f_i) + f_i \ln(f_i m_i) + f_i \sum_{j=1}^{\infty} c_{ij}' \ln c_{ij}' +$$

$$+(1-f_i)\sum_{j=1}^{\infty} c_{ij} \ln c_{ij}\Big] - y \ln\frac{z-2}{z}\Big\}$$

$$\Phi \approx -TS + E = -TS + A\Big\{zr_s eS_p + \frac{1}{2} zr_0 (\varepsilon_{pp} S_p + \varepsilon_{ss} S_s) +$$

$$+Pvr_0 + r_p \sum_{i=1}^{z} m_i \Big[\tau h \chi_i + f_i \sum_{j=1}^{\infty} c_{ij}'(\varepsilon_j' + \Delta\varepsilon) + (1-f_i)\sum_{j=1}^{\infty} c_{ij}\varepsilon_j\Big]\Big\}$$

$$y = \sum_{i=1}^{z} f_i m_i, \quad e = \frac{1}{2}(\varepsilon_{pp} + \varepsilon_{ss}) - \varepsilon_{ps} \tag{2.2}$$

Here, $\chi_i = 1 - \cos\theta_i$ for tension and $\chi_i = \cos\vartheta_i$ for compression. From (2.2) it is easy to obtain expressions for all the other thermodynamic potentials, the partial potentials of the components, the coefficients of thermal expansion, the compressibility, specific,heat, etc.

The equilibrium values of the parameters c_{ij}, c_{ij}', f_i, m_i and n_0 yield an extremum of the potential Φ. Considering Φ as a function of these parameters and the quantity y from (2.2) and taking into account the constraints (definition of y in terms of $f_i m_i$, conditions of normalization of c_{ij}, c_{ij}', f_i, and m_i), we obtain equations for the unknown parameters. As a result, for c_{ij} we obtain

$$c_{ij} = \exp\frac{-(j-1)\hbar\omega}{kT}\left(1-\exp\frac{-\hbar\omega}{kT}\right)^{-1} \tag{2.3}$$

The expression for c_{ij}' differs from (2.3) only in the substitution of ω' for ω. The equation for n_0 (r_0) has the form

$$\ln\frac{\nu_0}{1+\nu_0} + G(\nu_0, \nu_p, x_{pp}, x_{ss}, \Delta x, x_p, z) = 0$$

$$G = [z(1+\nu_0) - 2\nu_p]^{-2}\{x_{pp}(z-2)(z-2\nu_p)\nu_p + x_{ss} z(z-2\nu_p)(1-\nu_p) -$$

$$-2\Delta x z(z-2)\nu_p(1-\nu_p)\} + x_p + \nu_p(1+\nu_0)^{-1}$$

$$\nu_0 = \frac{r_0}{mr_p + r_s}, \quad \nu_p = \frac{mr_p}{mr_p + r_s}, \quad x_{pp} = \frac{z\varepsilon_{pp}}{2kT}, \quad x_{ss} = \frac{z\varepsilon_{ss}}{2kT}$$

$$x_p = \frac{Pv}{kT}, \quad \Delta x = \frac{ze}{2kT} \tag{2.4}$$

Here, ν_p may be regarded as a characteristic of the concentration of the system [7].

When $\nu_0 \ll 1$ Eq. (2.4) is easily solved, if it is assumed that $G \approx G_0 = G|\nu = 0$. We have

$$\nu_0 \approx e^{-G_0}(1 - e^{-G_0})^{-1} \approx e^{-G_0} \tag{2.5}$$

This formula gives a reasonable approximation at sufficiently large values of the x parameters in (2.4). In the same way, it is easy to investigate (2.4) on the assumption that $\nu_0 \gg 1$, which corresponds to very high system temperatures.

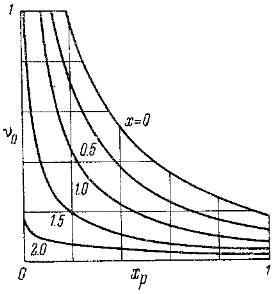

Fig. 1

It is easy to see that ν_0 decreases with increase in the dimensionless parameters x_{pp}, x_{ss}, and x_p and with decrease in the parameter Δx (i.e., the free volume increases with increase in temperature, weakening of the intermolecular interactions, deterioration of solvent quality, and decrease in pressure). The dependence of ν_0 on x_p in the region where the error of formula (2.5) may be large is given in Fig. 1 for various values of $x = x_{pp}$ (figures adjacent to the curves). We have considered only a block polymer, when z = 4. The effect of the concentration ν_p on ν_0 is more complicated. The relations between $g = -\ln\nu_0 - x_p$ and ν_p at various x_{pp} and x_{ss} are present in Fig. 2. Here, it has been assumed that $\Delta x = 0$; the solid curves in Fig. 2 correspond to the value $x_{pp} = 4$ and the values of x_{ss} indicated by the figures adjacent to the curves; the dashed curves have been plotted for $x_{ss} = 4$, the figures adjacent to the curves indicating the corresponding values of x_{pp}. Clearly, adding to the polymer a solvent of the same or lesser polarity causes an increase in free volume, while adding a solvent of much greater polarity leads to a decrease in free volume. The increase in the free volume of a mixture of a polymer and a solvent of the same polarity as the polymer content of the mixture decreases is obviously attributable to the fact that separation of the polymer segments is seriously impeded by the presence of intramolecular bonds between the segments of the same molecule.

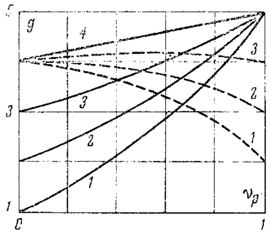

Fig. 2

For the quantities f_i, m_i, and y we have the equations

$$\ln\frac{f_i}{1-f_i} - \ln\frac{z-2}{z} + \ln\mu_i + \sigma_1 - \sigma_2 = 0, \quad \mu_i = \frac{f_i m_i}{y}, \quad \sum_{i=1}^{z} m_i = m$$
$$f_i\ln f_i + (1-f_i)\ln(1-f_i) + f_i\ln\mu_i - f_i\ln((z-2)/z) + f_i(\sigma_1-\sigma_2) + \alpha\chi_i = \lambda,$$
$$\sum_{i=1}^{z}\mu_i = 1, \quad \sigma_1 = \beta + \ln\left(1 - \exp\frac{-\hbar\omega'}{kT}\right), \quad \sigma_2 = \ln\left(1 - \exp\frac{-\hbar\omega}{kT}\right)$$
$$\alpha = \tau h/kT, \quad \beta = \Delta\varepsilon/kT \tag{2.6}$$

where λ is a certain constant (Lagrange multiplier). Combining, from (2.6) we obtain the expressions

$$(1-f_i)e^{\alpha\chi_i} = e^{\lambda} = \Lambda, \quad \mu_i = (1-f_i)(z-2)(f_i z)^{-1}e^{-\sigma_1+\sigma_2} \tag{2.7}$$

After the quantity Λ has been determined from the condition $\Sigma_i\mu_i = 1$, the parameters m_i can be found from the relations

$$m_i^* = \frac{m_i}{m} = \frac{\mu_i}{f_i}\left(\sum_{j=1}^{z}\frac{\mu_j}{f_j}\right)^{-1} \tag{2.8}$$

In an isotropic system $\mu_i = z^{-1}$, $f_i = f$ and $\Lambda = e^{\beta}(2 + e^{\beta})^{-1}$

$$f = \frac{(z-2)\,e^{-\sigma_1}}{e^{-\sigma_2} + (z-2)e^{-\sigma_1}} =$$

$$= \frac{(z-2)\,[1 - \exp(-\hbar\omega/kT)]\exp(-\Delta\varepsilon/kT)}{1 - \exp(-\hbar\omega'/kT) + (z-2)\,[1 - \exp(-\hbar\omega/kT)]\exp(-\Delta\varepsilon/kT)}$$

which coincides with the expression for f obtained in [5].

We note that within the framework of the model considered the parameters f_i and m_i do not depend on the free volume of the system, and when $\omega = \omega'$ they do not depend on the degree of development of the torsional vibrations either. Similarly, the population of the various vibrational levels and the free volume of the system do not depend on the mechanical stresses in the polymer.

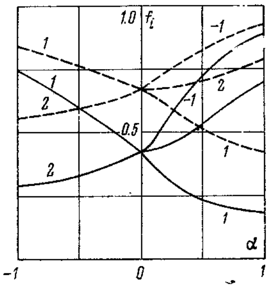

Fig. 3

The dependence of the parameters f_i and m_i^* on α at $\beta = 0$ (dashed lines) and $\beta = 1$ (solid lines) is presented in Figs. 3 and 4. In the calculations it was assumed that $z = 4$, the directions $i = 1$ and $i = -1$ being oriented along the line of action of the force, and the directions $i = 2$ and $i = -2$ at right angles to it. The values of i are indicated by the figures adjacent to the curves in Figs. 3 and 4, where positive values of α correspond to tension and negative values to compression. Obviously, in tension and compression the directions 2 and −2 are equivalent; in compression the directions 1 and −1 are also equivalent (the f_1 and f_{-1} curves and also the m_1^* and m_{-1}^* curves merge in the region of negative α). It can be seen from Figs. 3 and 4 that the extension or compression of an amorphous polymer is controlled by two simultaneous processes: firstly, by a redistribution of free isomers along the molecular chains with preservation of their total number; secondly, by a change in the relationship between folded and trans isomers, which proceeds differently in different directions, but is accompanied by a decrease in the total number of folded isomers and the appearance of a preferred bond orientation. These processes are considerably facilitated by an increase in the stiffness of the polymer molecules. The first process is accompanied by a change in the entropy of the system at constant energy, the second by a change in both entropy and energy. These conclusions are consistent with the results of the rotational isomerism theory of extension of individual molecular chains [10, 11] and also with the experiments described in [5]. We note that the efficiency of both these processes is independent of the quantities characterizing the intermolecular interactions, in particular, the solvent content of the system. This is easy to understand if it is kept in mind that all that has been said relates to equilibrium states attained after very prolonged application of the stress, but not to the rate at which these states are attained, which, of course, may depend on ν_p and the intermolecular interaction energies.

We also consider the equilibrium states at $\alpha \ll 1$, when it is possible to assume that the parameters characterizing these states differ by small amounts (indicated by a prime) from their equilibrium values in the isotropic system, i.e.,

$$f_i = f_{i0} + f_i', \quad \mu_i = \mu_{i0} + \mu_i', \quad m_i^* = m_{i0}^* + m_i^{*\prime}, \quad \Lambda = \Lambda_0 + \Lambda'$$

Using obvious expressions for the quantities in the isotropic state and the lattice geometry selected in constructing Figs. 3 and 4, from (2.7) and (2.8) we obtain

$$\Lambda' = \frac{\alpha e^{\beta}}{2 + e^{\beta}}, \quad f_i' = \frac{\alpha e^{\beta}}{2 + e^{\beta}} (\chi_i - 1), \quad \mu_i' = -\frac{\alpha (2 + e^{\beta})}{8} (\chi_i - 1)$$

$$m_i^{*\prime} = -{}^{1}/_{4}\alpha (1 + e^{\beta}) (\chi_i - 1) \tag{2.9}$$

Hence it is easy to see that the total number of folded isomers at small α is equal, correct to terms of the second order in α, to the number of folded isomers in the isotropic state; i. e., in the presence of relatively small forces only the first of the processes enumerated above is important and the resistance is purely an entropy effect. It is also clear from (2.9) that f_i' and m_i^* decrease with increase in temperature as follows from the "gas" theory of extension of chain molecules [5].

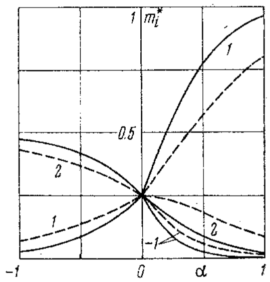

Fig. 4

The above formulas characterize the thermodynamics of the equilibrium states of the system at T ≥ T_g, At T < < T_g the previous expressions for the thermodynamic potentials are retained; however, the parameters c_{ij}, c_{ij}, f_i, m_i, and n_0 are calculated at the temperature T = T_g (see [9]).

§3. SOME APPLICATIONS

The proposed model differs importantly from existing models in two respects: first, in the simultaneous introduction of cells occupied by solvent molecules and vacant cells; second, in the explicit allowance for the effect of the external load on the structure of the equilibrium states of the polymer system. In order to illustrate the possibilities of this model (and other conceivable models of the same type) in accounting for a number of experimentally observed effects not yet explained by existing statistical theories, it is applied below to a series of particular problems of amorphous polymer physics: to the theory of solutions, to high-elastic deformation, and to phase transformations in polymer systems. In fact, all these problems represent broad independent regions of research, each of which has been the subject of a very large number of both theoretical and experimental studies. Therefore, we concentrate only on the qualitative aspects of certain selected phenomena that owe their origin to the presence of a free volume (holes) or an external load.

The shortcomings of the present theory of polymer solutions are discussed, for example, in [12]. The most serious of these shortcomings is the fact that in these theories volume changes are neglected. Other phenomena that contradict the Flory-Huggins theory [1] include: 1) the change in the interaction parameter χ (see Eq. (1.5)) with the concentration of the solution, this change being the more considerable the greater the difference between the polarities of the polymer and the solvent; 2) the negative entropies and heats of mixing observed when a polymer is dissolved or diluted in solvents of essentially different polarity; 3) the phase separation (thermodynamic instability) of polymer-solvent systems not only at low but also at high temperatures (the so-called "lower critical mixing temperature"). It is easy to see that the proposed model makes it possible to account for all these effects.

In fact, let us consider a stable polymer solution in an isotropic situation. On the basis of the results of section 2 its entropy and Gibbs function can be represented in the form

$$\begin{aligned} S = & -R (r_s \ln \varphi_s + r_0 \ln \varphi_0 + r_p \ln \varphi_p) - R r_p m \Big[1 - f \ln (z - 2) + f \ln f + \\ & + (1 - f) \ln (1 - f) + f \sum\nolimits_j c_j' \ln c_j' + (1 - f) \sum\nolimits_j c_j \ln c_j\Big] \\ \Phi = & -TS + \Big\{z r_s e S_p + {}^{1}/_{2}\, z r_0 (\varepsilon_{pp} S_p + \varepsilon_{ss} S_s) + \\ & + P v r_0 + r_p m \Big[f \sum\nolimits_j c_j' (\Delta\varepsilon + \varepsilon_j') + (1 - f) \sum\nolimits_j c_j \varepsilon_j\Big]\Big\} A \end{aligned} \tag{3.1}$$

The entropy of r_p moles of polymer in the amorphous state and r_s moles of pure solvent S° is equal to

$$S^{\circ} = S^{(p)} + S^{(s)}, \quad S^{(p)} = -R\,(r_0^{(p)} \ln \varphi_0^{(p)} + r_p \ln \varphi_p^{(p)}) -$$
$$- Rr_p m \left[1 - f \ln (z-2) + f \ln f + (1-f) \ln (1-f) + f \sum\nolimits_j c_j' \ln c_j' +\right.$$
$$\left. + (1-f) \sum\nolimits_j c_j \ln c_j \right], \quad S^{(s)} = -R\,(r_0^{(s)} \ln \varphi_0^{(s)} + r_s \ln \varphi_s^{(s)})$$
$$r_0^{(p)} = mr_p \nu_0^{(p)}, \quad r_0^{(s)} = r_s \nu_0^{(s)}, \quad \varphi_0^{(p)} = \frac{r_0^{(p)}}{mr_p + r_0^{(p)}}, \quad \varphi_0^{(s)} = \frac{r_0^{(s)}}{r_s + r_0^{(s)}} \qquad (3.2)$$

In the same way, it is easy to write expressions for the potential Φ° for pure polymer and solvent.

The expressions for the thermodynamic mixing parameters are easily obtained from (3.1) and (3.2):

$$\Delta V = R(r_0 - r_0{}^{(s)} - r_0{}^{(p)}), \quad \Delta\Phi = \Delta E - T\Delta S$$
$$\Delta S = R\left(r_s \ln \frac{\varphi_s^{(s)}}{\varphi_s} + r_p \ln \frac{\varphi_p^{(p)}}{\varphi_p} + r_0^{(s)} \ln \varphi_0^{(s)} + r_0^{(p)} \ln \varphi_0^{(p)} - r_0 \ln \varphi_0\right)$$
$$\Delta E = A\,\{zr_s e S_p + {}^1\!/_2\, z\,[\varepsilon_{pp}\,(r_0 S_p - r_0^{(p)} S_p^{(p)}) + \varepsilon_{ss}\,(r_0 S_s - r_0^{(s)} S_s^{(s)})]\} + P\Delta V,$$
$$S_s^{(s)} = \frac{r_s}{r_s + r_0^{(s)}}$$
$$S_p^{(p)} = \frac{[(z-2)\,m + 2]\,r_p}{[(z-2)\,m + 2]\,r_p + zr_0^{(p)}} \approx \frac{(z-2)\,mr_p}{(z-2)\,mr_p + zr_0^{(p)}} \qquad (3.3)$$

In ΔS from (3.3) it is possible to omit the term with c $r_p \ln(\varphi_p{}^{(p)}/\varphi_p)$ in view of the fact that $m \gg 1$; for simplicity it has been assumed that the excitation of torsional vibrations in the amorphous polymer does not depend on the amount of solvent. From (3.3) it is clear that in the presence of sharply different polarities of the components (i.e., essentially different x_{pp} and x_{ss}) the mixing entropy ΔS may well be negative. Moreover, an analysis shows that negative ΔS are possible even when the polarities of the polymer and the solvent are quite similar. Negative ΔS make a positive contribution to the quantity $\Delta\Phi$ which is greater in proportion to the temperature. Therefore at large T the quantity $\Delta\Phi$ may become positive, even if $\Delta E < 0$; this corresponds to disturbance of the thermodynamic stability of the solution. Under certain conditions the heat of mixing also becomes negative. As it is easy to show, using relation (2.4) and the first of equations (3.3), the change of volume ΔV is always negative, i.e., mixing is accompanied by compression, which is perfectly consistent with the experimental data of [12].

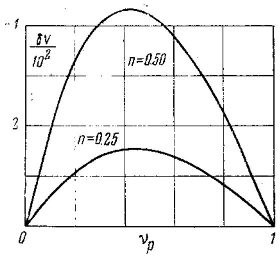

Fig. 5

For the purposes of a quantitative analysis we have everywhere assumed that $z = 4$, $x_p = 0$, while using model solutions of three types.

1. **Solution of a polymer in its own monomer.** In this case $x_{pp} = x_{ss}$, $\Delta x = 0$. The $\delta V = \delta V(\nu_p)$ curves are presented in Fig. 5, the figures adjacent to the curves denoting the dimensionless temperature n:

$$n = \frac{T}{T_0}, \quad \frac{2x_{pp}}{kT_0} = 1, \quad \delta V = \frac{\Delta V}{v\,(mr_p + r_s)} \qquad (3.4)$$

Clearly, δV is always negative and has a minimum as a function of ν_p corresponding approximately to half-concentrations. As n increases, the absolute value of δV rises very sharply; for example, at $n = 0.25$ the maximum of $|\delta V|$ is approximately 30 times greater than at $n = 0.75$. At sufficiently high temperatures the volume change reaches several percent. All this is in good agreement with experiment (see [7, 12]). We note that in these calculations the quantities ν_0, $\nu_0{}^{(p)}$ and $\nu_0{}^{(s)}$ were computed in the approximation (2.5).

2. Solution of a polar polymer in a nonpolar solvent. In this case, to be specific, we have assumed that

$\gamma x_{pp}(T_0) = x_{ss}(T_0) = 1$, $\gamma = 0.1$ and have employed the approximations that follow from (2.5) when $\nu_p \neq 0$:

$$\nu_0{}^{(s)} \gg \nu_0 \sim \nu_0{}^{(p)} \sim 0,\ \nu_0{}^{(s)} \approx (e^{1/n} - 1)^{-1}$$

The dependence of the reduced functions on ν_p and n was calculated on a computer:

$$\begin{aligned} \delta S &= \frac{\Delta S}{R\,(mr_p + r_s)} \approx (1 - \nu_p) \ln \left[\frac{1}{1 - \nu_p} \frac{1}{1 + \nu_0^{(s)}} \left(\frac{\nu_0^{(s)}}{1 + \nu_0^{(s)}} \right)^{\nu_0^{(s)}} \right] \\ \delta E &= \frac{\Delta E}{RT_0\,(mr_p + r_s)} \approx (1 - \nu_p) \left(-\nu_0^{(s)} + \frac{4\varkappa \nu_p}{2 - \nu_p} \right) \\ \delta \Phi &= \frac{\Delta \Phi}{RT_0\,(mr_p + r_s)} \approx \delta E - n \delta S, \quad \varkappa = \frac{\Delta x}{x_{ss}} \end{aligned} \tag{3.5}$$

3. Solution of a nonpolar polymer in a polar solvent. In this case, as before, it has been assumed that

$$x_{pp}(T_0) = \gamma x_{ss}(T_0) = 1, \quad \gamma = 0.1,\ \nu_0{}^{(p)} \gg \nu_0 \sim \nu_0{}^{(s)} \text{ and } \nu_0{}^{(p)} \approx (e^{1+1/n} - 1)^{-1},\ \nu_p \neq 1$$

The reduced functions have the form

$$\begin{aligned} \delta S &\approx -(1 - \nu_p)\ln(1 - \nu_p) + \nu_p \nu_0{}^{(p)} \ln (\nu_0{}^{(p)} / (1 + \nu_0{}^{(p)})) \\ \delta E &\approx \nu_p[-\nu_0{}^{(p)} + 4\varkappa(1 - \nu_p)\ (2 - \nu_p)^{-1}],\ \varkappa = \Delta x / x_{pp} \\ \delta \Phi &= \delta E - n \delta S \end{aligned} \tag{3.6}$$

The dependence of the reduced entropy δS for solutions of the second (solid curves) and third (dashed curves) types is presented in Fig. 6. It has been assumed that $\varkappa = 0$ and the figures adjacent to the curves indicate values of n from (3.4). It is clear that there are regions of negative δS at low concentrations (for solutions of the second type) and large ν_p (for solutions of the third type), these regions broadening considerably with increase in the temperature n. The analogous dependence of δΦ on ν_p is presented in Fig. 7 (same notation). The regions of positive δΦ are somewhat narrower than the regions of negative δS in view of the negativeness of δE. We note that the nature of these curves for a solution of the second type is, as it were, opposite to that of the curves for a solution of the third type. Phase diagrams of solutions of the second and third types, constructed on the basis of the calculations described, are shown in Fig. 8, where the regions of thermodynamic instability have been shaded. The region of instability adjacent to the straight line $\nu_p = 0$ relates to the solution of the second type, and the region adjacent to the straight line $\nu_p = 1$ relates to the solution of the third type. Despite the extreme simplicity of the lattice employed and the approximateness of the calculations, the shape of these regions is surprisingly close to the shape of the regions of instability observed experimentally at high temperatures [13]; the results of calculations are also in reasonable agreement with numerous experiments performed on very different systems (see, for example, the review in [14]). A simple analysis of relations (3.3) also shows that, in accordance with experiment, an increase in the order of the dissolved or diluted polymer [14] and, equally, an increase in the hydrostatic pressure in the system [15] tend to shift the curves in Fig. 8 in the direction of higher temperatures. From an analysis of relations (2.1) it follows that for the solutions considered the above-mentioned effects, "anomalous" from the standpoint of the Flory-Huggins theory, are intensified as the molecular weight of the polymer increases, which is also consistent with the experimental data [13–15].

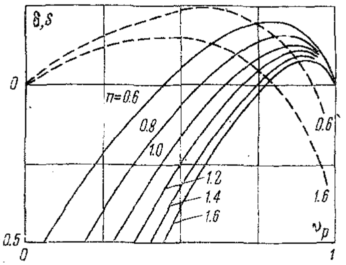

Fig. 6

It is easy to see that the principal reason for the deterioration of solubility with increase in temperature and the appearance of a lower critical mixing temperature is the fact that in this temperature region the coefficients of thermal expansion (determined by the change of free volume) of the polymer and the solvent are essentially different. In a number of cases the temperature of the solution may even be higher than the boiling point of the pure solvent [13]. The relatively expanded state of the solvent at high temperatures causes a negative contribution to δS (and also δV) when it is used to dilute a relatively compact polymer and vice versa, in accordance with the view expressed in [16].

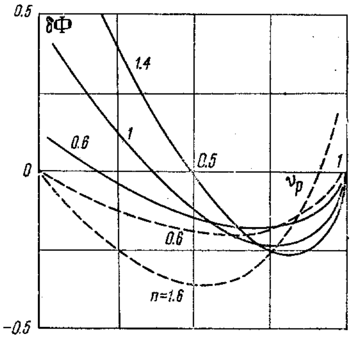

Fig. 7

These results show that at high temperatures phase separation may be observed even in very dilute solutions of a polar polymer in a nonpolar solvent and in nonpolar polymers containing small amounts of polar solvent. Experimental confirmation for dilute solutions at ordinary (room) temperature is reported in [17]. It may be that precisely this type of separation occurs in certain aqueous drag-reducing polymer solutions, causing "aging" of the polymer solution with the formation of a heterogeneous system of aggregations of more concentrated solution in almost pure solvent [18]. On the other hand, the appearance of an upper critical mixing point and a region of thermodynamic instability at low temperatures is caused not by entropy, but principally by energy factors. The change in the dependence of $\delta\Phi$ on ν_p for solutions of the second and third types (solid and dashed lines, respectively) with deterioration of the quality of the solvent (i.e., with increase in the parameter $\varkappa$ in (3.5), (3.6)) is illustrated in Fig. 9. Clearly, at sufficiently low temperatures when $\varkappa > 0$ regions of thermodynamic instability of the usual type appear. As the temperature increases, the effect of "nonathermicity" (nonzero $\varkappa$) monotonically decreases.

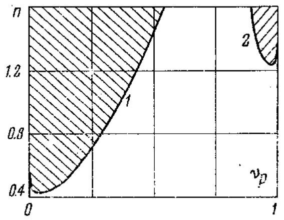

Fig. 8

We also consider the change of the interaction parameter χ with the concentration of the solutions. Equating relations (1.4) and (1.5), for the effective value of χ in the case when $\varkappa = 0$, i.e., $\omega\chi = 0$ according to the Flory-Huggins theory, we have the expression

$$\chi' = \frac{\chi}{A\nu_0} \approx \frac{1}{\nu_p(1-\nu_p)}(x_{pp}S_p + x_{ss}S_s), \quad \nu_0 = \nu_0(\nu_p) \tag{3.7}$$

The results of calculating the parameter χ' for solutions of the second (solid lines) and third (dashed lines) types at various temperatures n (figures adjacent to the curves) are presented in Fig. 10. The results are also consistent with experiment; for example, a rapid increase in χ with increase in the concentration of polar solvent has been observed in the case of solutions of polyisobutylene in pentane [13], polypropylene in ketones [14], etc.

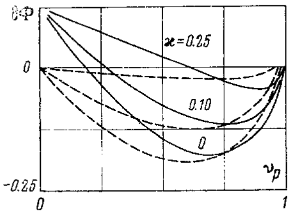

Fig. 9

Thus, the proposed model makes it possible to offer a perfectly natural explanation for all the principal deviations of the behavior of actual polymer solutions from that predicted by classical Flory-Huggins statistics merely from an analysis of the free volume of the system, without introducing any more refined ideas about the difference in the lengths of the intra- and intermolecular bonds, etc. These effects can be allowed for independently by means of the compressible cell and averaged potential methods proposed by Prigogine [19]. We note that attempts to apply these methods in the theory of polymer solutions have already been made, for example, in [12,16].

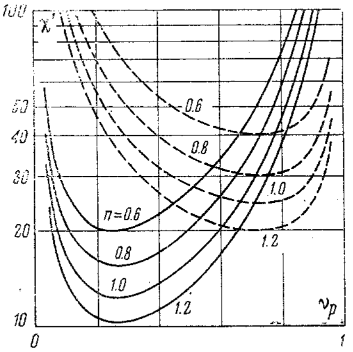

Fig. 10

We now consider the qualitative laws of polymer deformation. For simplicity, we confine ourselves to the case of extension of a block polymer (without solvent), neglecting the presence of holes and employing the same lattice geometry as in constructing Figs. 3 and 4. Clearly, if the tensile load τ increases relatively slowly, and the characteristic time of this process is much greater than the relaxation times of the system, the polymer will pass successively through a set of equilibrium states corresponding to increasing values of τ, so that the process of deformation is also an equilibrium process. Obviously, this behavior is typical at high temperatures, and in this case the structural characteristics of the states of the system (the fractions m_i^* of bonds oriented in different directions, the statistical weights of the folded isomers f_i, etc.) can be calculated by the method proposed in §2. In order to obtain the dependence of the relative elongation λ on the load τ it is merely necessary to be able to relate λ with the values of the above-mentioned structural characteristics. In principle, this can be done using the general methods of configurational statistics of polymer molecules described in [5]. Here, for the purposes of a qualitative estimate, we employ a simple approximate determination of λ assuming an approximately Gaussian distribution of the isomers along the molecular chains. We then have

$$\begin{gathered}\lambda(\tau) = L(0)^{-1}(L(\tau) - L(0)), \;\; L(\tau) \approx h(\sqrt{z_\tau - \Delta z_\tau} + \Delta z_\tau) \\ L(0) \approx h\sqrt{z_0}, \; Z_\tau = m_1(\tau) + m_{-1}(\tau), \;\; \Delta z_\tau = m_1(\tau) - m_{-1}(\tau)\end{gathered} \tag{3.8}$$

Introducing the coefficient $\varphi_1(\tau)$ and $\varphi_2(\tau)$, which can easily be computed from the expressions given in §2 we write

$$\begin{gathered}\Delta z_\tau = \varphi_1(\tau)m, \quad z_\tau - \Delta z_\tau = \varphi_2(\tau), \; \lambda(\tau) \approx \varphi(\tau)\sqrt{m} + \psi(\tau) \approx \varphi(\tau)\sqrt{m} \;\; (m \gg 1), \\ \varphi(\tau) = \varphi_1(\tau) / \sqrt{\varphi_2(0)}, \quad \psi^2(\tau) = \varphi_2(\tau) / \varphi_2(0)\end{gathered} \tag{3.9}$$

It follows from (3.9) that for equilibrium deformation the shape of the $\lambda(\tau)$ curves is similar to the shape of the $\varphi(\tau)$ curves. The equilibrium $\lambda(\tau)$ curves at three temperatures $T_0 > T_1 > T_2$ are shown qualitatively in Fig. 11 (curves 0,1,2, respectively). Clearly, the theory based on the proposed model differs from the "gas" theory of high elasticity of amorphous polymers [5,20] in three basic respects: the inclusion of energy changes during deformation resulting from the change in the total number of folded isomers (this effect was previously investigated in [10,11] for isolated chains), allowance for deviations from Gaussian distribution as the polymer molecules approach the state of maximum extension, and, moreover, allowance for cooperative effects in a lattice occupied by constrained polymer molecules, which, as it is easy to see, play a very considerable role in the development of large deformations. These distinctions are responsible for the deviation of the high-elastic strain curves in the direction of smaller λ as compared with the curves corresponding to the classical theory (a detailed physical discussion of the possible reasons for this deviation may be found in [5]). For example, in Fig. 11 the curve 1', describing the deformation of a polymer at a certain $m' < m$ at temperature T_1, is compared with a typical curve following from the gas theory (dashed line).

In reality, the high-elastic strains of actual polymers are usually essentially nonequilibrium, equilibrium being attained only in the limit, when the load τ varies slowly, or at very high temperatures (see, for example, [21]).

There have been numerous attempts to take this nonequilibrium effect into account, both phenomenological, within the framework of the theory of viscoelasticity, based on the introduction of a relaxation spectrum, and physical, associated with the construction of special models. An example is the work of Ciferri and Hermans [22], in which the nonequilibrium effects are described by introducing certain "labile" nodes in the molecular network (entanglements, etc.). Here, we examine a simple model, in which the presence of intermolecular interactions in the system is responsible for the formation of labile nodes.

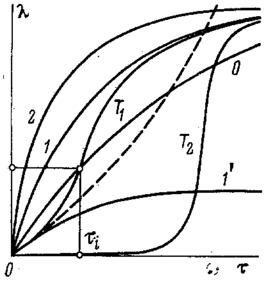

Fig. 11

In accordance with Eyring's theory of absolute reaction rates [23], the probability of the fluctuational displacement of a segment of a polymer molecule acted upon by a force τ can be represented in the form

$$q(\tau) \sim e^{-a},\ a = [(z-2)\varepsilon' - \tau l]\ (kT)^{-1},\ \varepsilon' \sim \varepsilon_{pp},$$

$$l \sim h \tag{3.10}$$

Here, $(z - 2)\varepsilon' - \tau l$ is the effective potential barrier that must be overcome to permit the displacement in question. The mean dimension of the portion of a molecular chain, expressed as the number of segments μ, that can relatively rapidly change its configuration in a force field, is estimated as follows:

$$\mu \approx \sum_{\mu=0}^{\infty} \mu' q(\tau)^{\mu'} = \frac{e^{-a}}{(1-e^{-a})^2} \tag{3.11}$$

The dependence of μ and τ at various temperatures is represented qualitatively in Fig. 12a. As $\tau \to \tau_* = (z - 2)\varepsilon' l^{-1}$ these curves go to infinity. However, if μ is bounded above by the size of the molecules (or the spacing between crosslinks) m, the true $\mu(\tau)$ curves approach the straight line $\mu = m$ (dashed lines in Fig. 12a). For example, at the temperature T_1 let $\mu(0) = m'$ (curve 1' in Fig. 11). As τ increases, the size of the autonomous chains $\mu(\tau)$ increases in accordance with the curves in Fig. 12a, and the $\lambda(\tau)$ curve deviates from curve 1' in the direction of curve 1 in Fig. 11 corresponding to $\mu = m$, acquiring a characteristic S shape. At $\tau \sim \tau_*$ the deformation curve T_1 and curve 1 almost merge (we note that if m represents the length of the molecules in a polymer without crosslinks, at high values of τ plastic irreversible deformation or viscous flow, which, of course, is not described by the curves in Fig. 11, may be observed). It is easy to see that curve 1 in Fig. 11 is similar in shape to the experimental curves [5].

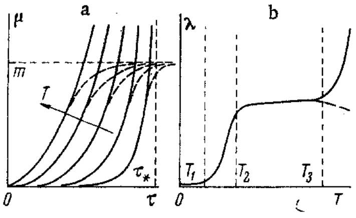

Fig. 12

Let us consider the deformation of the same polymer at other temperatures. At $T_2 < T_1$ let the polymer be in the glassy state, so that at small τ the deformation is basically determined only by the change in the lengths of the intra- and intermolecular bonds, while the mobility of the units of the molecular chain is limited and μ from (3.11) is also very small. As τ increases in the region $\tau \sim \tau_*$ the quantity μ from (3.11) should increase sharply, causing an equally sharp increase in the deformation $\lambda(\tau)$ (see the curve marked T_2 in Fig. 11). Obviously, this corresponds to the forced elastic deformation of the glassy polymer at high stresses.

The model proposed also makes it possible to explain the phenomenon of thermoelastic inversion associated with the stretching of a polymer [5]. As an example, suppose that at the temperature $T_0 > T_1$ a polymer is stretched under almost equilibrium conditions, i.e., in accordance with curve 0 in Fig. 11. It is easy to see that when $\lambda < \lambda_i$ and $\tau < \tau_i$ raising the temperature from T_i to T_0 causes a decrease in the stress τ at λ = const or an increase in λ at τ = const. In the region $\lambda > \lambda_i$, $\tau > \tau_i$ the opposite is true.

The curves in Figs. 11 and 12a make it possible to construct the thermomechanical curves of the polymer—the dependence of λ on T at constant τ. An example of such a curve is presented in Fig. 12b; its shape is similar to the shape of the corresponding experimental curves [7]. At large T viscous flow may develop in a noncrosslinked polymer (solid line) or (in the case of a crosslinked polymer) there may be a certain decrease in λ with further increase in temperature (dashed line in Fig. 12b).

We note that in the deformation of amorphous polymers a certain role is also played by effects associated with the competition between individual molecules in the process of spatial orientation, which make an additional contribution to the total entropy of the system. These effects were examined in [24]; we note that they can easily be taken into account within the framework of the proposed model.

Let us briefly discuss the effect of the parameters of the system and the external load on phase transformation in amorphous polymers. The theory of equilibrium crystallization and melting of polymers was developed by Flory [4]; taking the torsional vibrations into account made it possible to obtain results very similar to those observed experimentally for polyethylene [5]. Certain important new factors, not described in [4, 5], are taken into account in the proposed theory: these are the presence of a free volume in polymer solutions and the change in the structure of the equilibrium states in the direction of an intensification of orientation in the presence of an external load. An analysis shows that the presence of a free volume somewhat facilitates the random packing of the polymer molecules and reduces the melting point or crystallization point in equilibrium processes. On the other hand, the preferred orientation of the molecules during deformation (especially in tension and to a lesser extent in compression) reduces the number of permissible random packings and increases the Gibbs function of the system, thereby raising the phase-transition temperature. This is confirmed by the experimental data on the forced crystallization of stretched rubbery materials and is consistent with the accepted view [5].

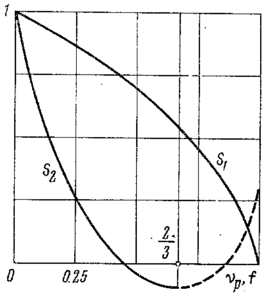

Fig. 13

There is as yet no unanimity concerning the nature of the glass-transition effect and the corresponding temperature T_g, apparently because of the ambiguity of the various methods of determining T_g and the effect on them of the kinetic characteristics of the processes used in different experiments. Thus, for example, some authors deny that glass transition is essentially a second-order phase transformation (for example, [5, 25]), whereas others ascribe to it the properties of a phase transition of not only second, but first order [26]. Here, by the temperature T_g we understand the temperature of an Ehrenfest second-order phase transition in accordance with the glass-transition theory of Gibbs and Di Marzio [9], as mentioned at the end of §1. We note that most of the arguments of the partisans of a purely kinetic approach to the glass-transition problem enumerated, for example, in [5], confirm rather than refute the point of view expressed in [9]; in particular, the basic argument concerning the dependence of the glass-transition temperature, determined experimentally, on the rate at which the experiments are carried out is directly related with the hypothesis of [9] and, in fact, follows from it. Moreover, the true phase transition may be masked in the experiments not only by the influence of kinetic factors but also, for example, as a result of the degeneracy of the torsional vibrations, which persists even in the glassy state as the temperature is further reduced, as noted by Ueberreiter [26].

The relations given in §§1 and 2 make it possible to estimate the effect on T_g of a variety of factors. Here we consider only two particularly significant examples. We first investigate the dependence of T_g on the concentration ν_p of an isotropic solution of a polymer in its own monomer (solution of the first type). Neglecting, for simplicity, the free volume and taking $z = 4$, after simple computations we obtain the estimate

$$S' = k \ln W' \sim \Psi_1(v_p) - \Psi_2(f), \quad \Psi_1 = -v_p^{-1}(1 - v_p)\ln(1 - v_p)$$
$$\Psi_2 = 1 + f \ln f + (1 - f)\ln(1 - f) - f \ln(z - 2)$$

The functions Ψ_i are presented in Fig. 13; when $\Delta\varepsilon > 0$ we have $f < 2/3$, so that in the region $f > 2/3$ the curve $\Psi_2(f)$ is meaningless (dashed line in Fig. 13). According to [9] glass transition occurs at $S' \approx 0$, i.e., $\Psi_1(\nu_p) \approx \Psi_2(f_g)$, where $f_g = f_g(\nu_p)$ is the root of the latter equation. The quantity $f_g(\nu_p)$ is easily determined from Fig. 13; from the expression for f in §2 there then follows

$$\frac{kT_g}{\Delta\varepsilon} = -\ln^{-1}\left(\frac{1}{z-2}\frac{f_g(v_p)}{1 - f_g(v_p)}\right) \tag{3.12}$$

which finally gives the temperature T_g. The dependence of T_g (3.12) on ν_p is presented in Fig. 14. Clearly, in accordance with experiments on polymers that swell in good solvents [17], at sufficiently large ν_p the temperature T_g depends almost linearly on ν_p. In the presence of swelling in poor solvents, starting from a certain ν_p, the thermodynamic stability of the system is disturbed and separation takes place, so that the plasticizer introduced begins to play the part of an interstructural lubricant [17]. In this case the fall of T_g ceases, which is conventionally represented in Fig. 14 by the dashed line AB, a jump B → C being possible when thermodynamic stability is attained in the region of comparatively small ν_p. We note that the temperature T_g thus determined relates to the stable phase in the heterogeneous system obtained; for this system as a whole a formula of the (3.12) type is incorrect, and an interstructural lubricant may cause a fall in the effective glass-transition temperature even in the region of constancy of T_g for homogeneous structures A–B.

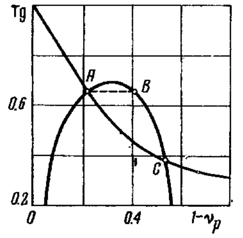

Fig. 14

As a second example we will consider the dependence of the glass-transition temperature T_g', determined from the beginning of forced elasticity of the glassy polymer, on the tensile load τ. According to (3.11), at sufficiently low temperatures forced elasticity begins at

$$(z - 2)\varepsilon' - \tau l \sim kT_g', \text{ т. е. } T_g' = C_1 - C_2\tau, \quad C_i = \text{const}$$

which corresponds exactly to the empirical equations for various polymers established in [27].

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