Effect of concentration of active solution on the "melting" of a double polymer chain

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The problem is considered of the influence of an active solution on the "melting" of a double polymer chain of the type of the DNA molecule. A model is used in which the dissolved substance can become joined to split sections of the double chain, and only one molecule from the solution is joined to an individual element of the chain. The exact partition functions for such a system are calculated. The dependences of the phase-transition temperature on the concentrations of the low-molecular substance at the macromolecule and in the substance are obtained and analyzed. It turned out that the dependence of the transition temperature on the concentration is nonmonotonic and nonunique at certain definite values of the parameters of the problem.

INTRODUCTION

Theoretical questions related to the phase-transition problem in a double polymer chain (such as the DNA molecule) have been discussed many times in the literature [1-4]. It was ascertained that the process of splitting of a long double molecule into individual filaments is under certain conditions [1,2] indeed a phase transition. The indicated conditions reduce to realization of a definite number of independent configurations that individual filaments of the split section of the molecule can assume. We start from the assumption that these conditions are satisfied and consequently that a phase transition of the type of "melting" of DNA takes place.

With the question so formulated, it is of interest to establish the dependence of the phase-transition temperature on the external conditions. The most significant manifestation of external actions on the system considered is the chemical activity of the solution in which the polymer chain is located.

1. FORMULATION OF MODEL

In this paper, using a very simple model, we investigate a phase transition in a double linear chain, the split sections of which interact with molecules of dissolved matter (of low molecular weight). It seems to us that the model employed pertains directly to synthetic DNA in solutions of salts [5], and also describes qualitatively the state of a DNA molecule in a formaldehyde solution [6].

We consider a long molecule consisting of two complementary filaments. We assume that the macromolecule is immersed in a solution of a certain low-molecular substance, say an acid, a salt, alcohol, etc., the molecules of which can interact with the double chain. The sections of the molecules can be in two states: 1) bound (double-braid section) and 2) split. We assume that the elements of the chain in the bound state do not interact with the molecules of the dissolved matter, since they have no free bonds (their hydrogen bonds are saturated). Thus, each element of the double section can be in only one state. The binding energy between the complementary elements of two filaments will be designated by $-V_0$ ($V_0 > 0$), and the corresponding statistical weight of the double section will be designated ω_1.

In the split state, the two filaments of the macromolecule diverge, are not connected with each other by hydrogen bonds, and can become attached to molecules from the solution. We assume that only one molecule of the dissolved matter attaches itself to one element of each filament. This is approximately the behavior of the DNA molecule in the formaldehyde solution [6]. Thus, each element of the filament of the split section can be in two states: in state a, if no molecule from the solution is attached to it, or in state b, if one molecule is attached (Fig. 1). The energy per filament element in the state a will be assumed equal to zero, and the energy of the element in state b will be designated by $-W_0$ ($W_0 > 0$). The molecules attached to two neighboring elements of one filament can interact with each other. The energy of this interaction is designated W_1. We note that W_1 can, in principle, be either positive or negative, depending on whether the repulsion or attraction forces between the attached molecules prevail. Interaction between attached molecules that are not near neighbors on the linear chain will be neglected.

The statistical weight of an element of an individual filament of the split section of the chain will be assumed equal to $(\omega_2)^{1/2}$. We denote by σ_n^r the state of the element numbered n (n numbers the elements of an individual filament and is reckoned from one edge of the macromolecule 1)) belonging to the filament with number r ($r = 1, 2$). We assume that $\sigma_n^r = 0$ in the state a and that $\sigma_n^r = 1$ in the state b. The energy (Hamiltonian) of m elements of an individual filament of the split section can then be represented in the form

$$H_m{}^r=\sum_{n=1}^{m-1} W_1\sigma_n{}^r\sigma_{n+1}^r-\sum_{n=1}^{m}\sigma_n{}^r W_0=\sum_{n=1}^{m-1}E_{n,\,n+1}^r-\frac{1}{2}W_0(\sigma_1{}^r+\sigma_m{}^r), \tag{1}$$

$$E_{n,\,n+1}^r=-\frac{1}{2}W_0(\sigma_n{}^r+\sigma_{n+1}^r)+W_1\sigma_n{}^r\sigma_{n+1}^r.$$

For brevity, as before,[4] we call the split internal section of the double molecule the "ring" and the edge section the "tail." We shall consider henceforth two

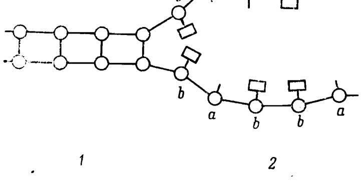

FIG. 1

cases that differ in the description of the boundary elements of the tail and of the ring. In the former case (C1) we assume that the impurity molecules interact with one another only along each of the filaments. In the latter case (C2) we assume that the attached molecules belonging to different filaments also interact with one another in those places where the rings and tail go over into coupled sections. In Fig. 1, for example, the two outermost left-hand impurity molecules can interact with each other. Assuming the nature of this interaction to be the same as on each of the filaments, we denote its energy by W_1.

2. CALCULATION OF PARTITION FUNCTION

To determine the thermodynamic properties of the system, it is convenient to use the grand canonical ensemble method [2,7]. We introduce the chemical potential μ of the complementary pairs of filament elements and the chemical potential μ_1 of the attached molecules on the polymer chain. The partition function of the grand canonical ensemble can then be represented in the form

$$Z(\mu,\mu_1)=\sum_{N=1}^{\infty}\sum_{K=0}^{2(N-1)}\exp\{\beta[\mu(N-1)+\mu_1 K]\}Z_0(N,K), \tag{2}$$

where $\beta=(kT)^{-1}$ and $Z_0(N, K)$ is the partition function of a double chain consisting of N pairs of elements, in which K molecules from the solution are attached to the split sections of the filaments.

The breakdown of the macromolecules into split and paired sections, which is needed for the calculation of the partition function, can be carried out in the same manner as in the earlier studies [2,4]. It is easy to verify that the presence of foreign molecules attached to the split sections of the chain does not change the earlier calculation [4]. It is therefore possible to use the results of that reference directly, representing the sought partition function in the form

$$Z(\mu,\mu_1)=\frac{e^{u/2}(e^{u/2}+Z^F(\mu,\mu_1))}{1-tz_1-Z^{II}(\mu,\mu_1)}, \tag{3}$$

where, in a departure from [4], all the quantities are numbers rather than matrices, and their sequence in the product can be arbitrary. The notation in (3) is the following:

$$t=e^{\beta\mu},\qquad u=\beta V_0,\qquad z_1=\omega_1 e^{u}. \tag{4}$$

$te^{u/2}Z^F(\mu, \mu_1)$ is the partition function of the grand canonical ensemble of a double, fully split chain joined only at one extreme point. This quantity describes the contribution made to the total partition function by the edge split section (tail). The quantity $tz_1Z^{II}(\mu, \mu_1)$ is the partition function of the grand canonical ensemble for a split double chain joined only at the edge elements. It describes the contribution of the rings to the total partition function.

We proceed now to calculate the partition functions $Z^{II}(\mu, \mu_1)$ and $Z^F(\mu, \mu_1)$ in the two indicated cases. In C1 the summation over the states of each of the filaments in the rings can be carried out independently, so that the partition function of such a section can be represented in the form of a product of the partition functions of each of the filaments. As a result we obtain

$$Z^{II}(\mu,\mu_1)=\sum_{m=0}^{\infty}A_{m+2}t^{m+2}\{\mathrm{SAE}[\hat{\gamma}_1(\hat{z}_2)^m\hat{\gamma}_2]\}^2, \tag{5}$$

where $\mathrm{SAE}(\hat{M})$ is the sum of all the elements of the matrix $\hat{M}$. The indices of the matrices are determined by the states of the corresponding elements of each of the filaments of the double chain. Just as in the other papers [1,2,4,8], the coefficient A_m determines the number of possible configurations of a double split section of a chain (ring) consisting of $m-1$ pairs of elements. In accord with the statements made in the Introduction, we assume that the series ΣA_m converges.

For the matrix $\hat{\gamma}_1$ that describes the transition from the boundary coupled elements to the split states of each of the filaments we have

$$\hat{\gamma}_1=(\gamma\omega_2)^{1/2}e^{u/4}\begin{pmatrix}1 & e^{\varepsilon}\\ 0 & 0\end{pmatrix}, \tag{6}$$

where $\epsilon=\frac{1}{2}\beta(\mu_1+W_0)$ and $(\gamma\omega_2)^{1/2}$ is the statistical weight of the union of the links at the junction point of two different sections. For the matrix $\hat{z}_2$, which describes an individual (free) filament, we obtain

$$\hat{z}_2=\omega_2^{1/2}\begin{pmatrix}1 & e^{\varepsilon}\\ e^{\varepsilon} & e^{2(\varepsilon+\varepsilon_1)}\end{pmatrix}, \tag{7}$$

where $\epsilon_1=-\frac{1}{2}\beta W_1$. Finally, for the matrix $\hat{\gamma}_2$, which is due to the same cause as the matrix $\hat{\gamma}_1$, we have

$$\hat{\gamma}_2=(\gamma\omega_2)^{1/2}e^{u/4}\begin{pmatrix}1 & 0\\ e^{\varepsilon} & 0\end{pmatrix}. \tag{8}$$

As seen from (5), (6), and (8), in C1 the statistical matrix of each of the filaments of a ring of arbitrary length has only one nonzero element after summation over all the internal states. This is a result of the fact that the split section is bounded by linked elements that have only one state.

For the partition function $Z^F(\mu, \mu_1)$ we have

$$Z^F(\mu,\mu_1)=\sum_{m=0}^{\infty}t^{m+1}\{\mathrm{SAE}[\hat{\gamma}_1(\hat{z}_2)^m\hat{z}_f]\}^2, \tag{9}$$

$$\hat{z}_f=\begin{pmatrix}1 & 0\\ 0 & e^{\varepsilon}\end{pmatrix}. \tag{10}$$

The matrix $\hat{z}_f$ is a result of symmetrization of the energy in (1) and is connected with the last pair of elements of the tail.

It is seen from (6), (9), and (10) that the statistical matrix of each of the filaments of the tail has, generally speaking, two nonzero elements. This is a consequence of the fact that each of the outermost elements of the tail can be in two states.

To obtain $\hat{Z}(\mu, \mu_1)$ it is convenient to use a representation in which the matrix $\hat{z}_2$ is diagonal. For the transformation that brings $\hat{z}_1$ to the diagonal form $\hat{\Lambda}$ we obtain

$$\hat{\Lambda}=\hat{S}^{-1}\hat{z}_2\hat{S}=\begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix},\quad \hat{S}=g\begin{pmatrix}s & 1\\ -1 & s\end{pmatrix}; \tag{11}$$

$$g=(1+s^2)^{-1/2},\qquad s=\varkappa_2 e^{\varepsilon_1}-e^{-\varepsilon}, \tag{12}$$

$$\lambda_1=\omega_2^{1/2}\varkappa_1 e^{\varepsilon+\varepsilon_1},\quad \lambda_2=\omega_2^{1/2}\varkappa_2 e^{\varepsilon+\varepsilon_1}, \tag{13}$$

$$\begin{gathered}\varkappa_1=\mathrm{ch}(\varepsilon+\varepsilon_1)-[\mathrm{sh}^2(\varepsilon+\varepsilon_1)+e^{-2\varepsilon_1}]^{1/2},\\ \varkappa_2=\mathrm{ch}(\varepsilon+\varepsilon_1)+[\mathrm{sh}^2(\varepsilon+\varepsilon_1)+e^{-2\varepsilon_1}]^{1/2}.\end{gathered} \tag{14}$$

Substituting the quantities determined above in (3) and performing the matrix operations, we obtain the sought partition function

$$\begin{aligned}Z(\mu,\mu_1)=\Delta_1^{-1}\Big\{1+\gamma g^4 t\Big[&s^2(s-e^{\varepsilon})^2\lambda_1^2/(1-t\lambda_1^2)\\ &+2s(s-e^{\varepsilon})(1+se^{\varepsilon})\frac{\lambda_1\lambda_2}{1-t\lambda_1\lambda_2}+\frac{\lambda_2^2}{\omega_2}\frac{\lambda_2^2}{1-t\lambda_2^2}\Big]\Big\},\end{aligned} \tag{15}$$

where

$$\Delta_1(\mu,\mu_1)=e^{-u}-t\omega_1-\gamma^2 g^4\sum_{m=2}^{\infty}A_m t^m(s^2\lambda_1^m+\lambda_2^m)^2. \tag{16}$$

Formulas (15) and (16) completely determine the partition function of the grand canonical ensemble in C1 as a function of μ, μ_1, and T.

We consider now C_2. The interaction of the impurities on the outermost pairs of the complementary elements of the rings and of the tail are described by the matrix $\gamma\omega_2^{1/2}e^{u/2}z_2$, where γ has the same meaning as in formulas (6) and (8). The states of the rings can now be fully summed in matrix fashion. By way of illustration we write down the partition function of a ring consisting of m pairs of split elements:

$$Z_m^{\mathrm{II}}=A_{m+1}(\gamma\omega_2^{1/2}e^{u/2})^2t^{m+1}\mathrm{Sp}(\hat{z}_2^{2m}). \tag{17}$$

Thus

$$Z^{\mathrm{II}}(\mu)=\gamma^2\omega_2e^u\sum_{m=2}^{\infty}A_mt^m(\lambda_1^{2m-2}+\lambda_2^{2m-2}). \tag{18}$$

It is convenient to use the same method to sum the states of a tail containing m pairs of split elements:

$$Z_m^F=\gamma\omega_2^{1/2}e^{u/2}\mathrm{SAE}(z_f\hat{z}_2^{2m-1}z_f). \tag{19}$$

Summing (19) over m and substituting the result together with (18) in (3), we arrive at a final expression for the partition function:

$$Z(\mu,\mu_1)=\Delta_2^{-1}(\mu,\mu_1)\Big\{1+\gamma\omega_2^{1/2}g^2t\Big[(s-e^{\varepsilon})^2\frac{\lambda_1}{1-t\lambda_1^2}+(1+se^{\varepsilon})^2\frac{\lambda_2}{1-t\lambda_2^2}\Big]\Big\}, \tag{20}$$

$$\Delta_2(\mu,\mu_1)=e^{-u}-t\omega_1-\gamma^2\omega_2\sum_{m=2}^{\infty}A_mt^m(\lambda_1^{2m-2}+\lambda_2^{2m-2}). \tag{21}$$

Formulas (20) and (21) determine the partition function of the grand canonical ensemble in C2 as a function of μ, μ_1, and T.

3. ANALYSIS OF PHASE TRANSITION

We seek to determine the equation of the phase-transition curve from the condition that the chemical potentials of the different phases of the macromolecule be equal. The chemical potential is determined in the grand-canonical-ensemble method by the condition (see, e.g., [2,7]):

$$N=-\frac{\partial\Omega}{\partial\mu},\quad \Omega=-kT\ln Z(\mu,\mu_1). \tag{22}$$

where N is the number of complementary pairs of elements of the macromolecule. As $N\to\infty$ (we are interested in precisely this case), Eq. (22) goes over into

$$\frac{\partial\Omega}{\partial\mu}=-\infty. \tag{23}$$

It can easily be concluded from examination of the partition functions (15) and (20) that the chemical potential μ defined by the solution of (23) is determined either from the condition

$$t\lambda_2^2=1, \tag{24}$$

or from the equation

$$\Delta(\mu,\mu_1)=0, \tag{25}$$

where $\Delta(\mu,\mu_1)$ is given by (16) or (21) for C1 or C2, respectively[2].

Inasmuch as the condition (24) is connected with the largest root of the matrix $\hat{z}_2$, it follows that the function $\mu(T)$ obtained from (24) is the chemical potential of the phase of the fully split chain (denatured phase). The solution of (25) yields the chemical potential of a phase in which there exist simultaneously coupled and internal split sections of the chain (double-chain phases). The phase-transition temperature is the temperature at which the conditions (24) and (25) are satisfied simultaneously.

We introduce the concentration η of the impurity on the chain as the ratio of the number of elements that attach molecules to themselves from the solution to the total number of elements of the macromolecule. Then

$$\eta=\frac{1}{2}\frac{\partial Z}{\partial\mu_1}\Big/\frac{\partial Z}{\partial\mu}. \tag{26}$$

We assume, as usual [1,2,4,8] that the coefficients A_m that enter in (16) and (21) behave at large m like m^{-p}, where $1<p\leq 2$. Then the series

$$\psi(x)=\sum_{m=2}^{\infty}A_mx^m\quad(x\leqslant 1) \tag{27}$$

converges at all x, including x = 1, and the derivative $\psi'(z)$ becomes infinite at x = 1. Therefore the derivatives of $\Delta(\mu,\mu_1)$, both with respect to μ_1 and with respect to μ, become infinite at the phase-transition point[3]. In view of this fact, it is easily verified that we have on the phase equilibrium curve

$$\eta=\frac{1}{2\lambda_2}\Big(\frac{\partial\lambda_2}{\partial\varepsilon}\Big). \tag{28}$$

In the region where the denatured phase exists, the concentration η is also determined by (28).

Eliminating the chemical potentials μ and μ_1 from (24), (25), and (28) we can obtain the dependence of the phase-transition temperature on the concentration η. The dependence of μ_1 on η and T can be obtained directly from (13) and (28):

$$e^{\varepsilon+\varepsilon_1}=\frac{[(2\eta-1)e^{-\varepsilon_1}+B]}{2[\eta(1-\eta)]^{1/2}},$$
$$\varepsilon={}^1/_2\beta(\mu_1+W_0),\quad \varepsilon_1=-{}^1/_2\beta W_1,\quad B=[4\eta(1-\eta)+(2\eta-1)^2e^{-2\varepsilon_1}]^{1/2}. \tag{29}$$

From (29) follows a natural dependence of the chemical potential μ_1 on the concentration in the limiting case $\eta\ll 1$. Indeed, substituting in (29) the explicit expressions for ϵ and ϵ_1, we easily obtain

$$\mu_1=kT\ln\eta-W_0. \tag{30}$$

On the other hand, if $W_1=0$, then we have at all concentrations

$$\mu_1=kT\ln\frac{\eta}{1-\eta}-W_0. \tag{31}$$

We use the definition of the transition temperature, and also relation (29). Then the phase-transition curves $T=T(\eta)$ are determined implicitly by transcendental equations that are different for C1 and C2. For the first case (C1) we have

$$e^{-u}=\frac{\omega_1}{\lambda_2^2}+\gamma^2\sum_{m=2}^{\infty}A_m\Big[1-\eta+\eta\Big(\frac{\lambda_1}{\lambda_2}\Big)^m\Big]^2 \tag{32}$$

and for the second (C2)

$$e^{-u}=\frac{\omega_2}{\lambda_2^2}\Big\{\frac{\omega_1}{\omega_2}+\gamma^2\sum_{m=2}^{\infty}A_m\Big[1+\Big(\frac{\lambda_1}{\lambda_2}\Big)^{2m-2}\Big]\Big\}, \tag{33}$$

where λ_1 and λ_2 are expressed in terms of the concentration η as follows:

$$\lambda_2=\frac{\omega_2^{1/2}}{2(1-\eta)}\{2(1-\eta)+(2\eta-1)e^{-2\varepsilon_1}+Be^{-\varepsilon_1}\},$$
$$\frac{\lambda_1}{\lambda_2}=\frac{B-e^{-\varepsilon_1}}{B+e^{-\varepsilon_1}}. \tag{34}$$

In the case $\eta=0$, Eqs. (32) and (33) coincide and go over in natural fashion to the previously known [1,2,4] equation

$$e^{-u}=\omega_1/\omega_2+\gamma^2\psi(1). \tag{35}$$

At $\eta \ll 1$, Eqs. (32) and (33) can be solved explicitly (at constant γ). It follows from these solutions that for definite ratios of the parameters of the problem (for example, at $W_1 < 0$ and $|W_1| \to \infty$), the plots of $T = T(\eta)$ go through a minimum in the region of small η.

The explicit dependence of the transition temperature on η for arbitrary W_1 can also be obtained in the vicinity of the point $\eta = 1$. Indeed, at $1-\eta \ll 1$ we obtain in C1

$$kT(\eta)=(-V_0+2W_1)/2\ln(1-\eta) \qquad (W_1\leqslant 0), \tag{36}$$

$$kT(\eta)=-V_0/2\ln(1-\eta) \qquad (W_1>0). \tag{37}$$

For C_2, the phase-equilibrium curve reaches the values $\eta = 1$ only at $W_1 \leq V_0/2$. In this case we obtain for $1-\eta \ll 1$

$$kT(\eta)=(-V_0+2W_1)/2\ln(1-\eta). \tag{38}$$

For C2 at $W_1 > V_0/2$, the denatured phase is always realized at the point $\eta = 1$.

The characteristic feature of the relations (36)—(38) is the presence of a vertical tangent to the curve $T = T(\eta)$ at the point $\eta = 1$, with $T(1) = 0$.

If there is no interaction between the attached molecules ($W_1 = 0$), then Eqs. (32) and (33) coincide at all concentrations, and the dependence of the transition temperature (curves 1 on Figs. 2 and 3) can be represented in explicit form:

$$T(\eta)=\frac{T_0}{1-2(kT_0/V_0)\ln(1-\eta)}. \tag{39}$$

Let us examine the case C1 in greater detail. If $W_1 < 0$ (attraction between the impurities), then the $T = T(\eta)$ curves lie above the corresponding curve at $W_1 = 0$ (curves 2 and 3 in Fig. 2). In the case when $W_1 < 0$ and $|W_1| \to \infty$ the phase-equilibrium temperature tends to a straight line $T = T_0$ in the interval $0 < \eta < 1$, and assumes the values $T(0) = T_0$ and $T(1) = 0$ on the edges. The minimum of the $T = T(\eta)$ curve in the region of small η shifts to the left at $W_1 < 0$ with increasing $|W_1|$, and tends to the point ($\eta = 0$, $T = T_0$) as $|W_1| \to \infty$.

If $W_1 > 0$ (the impurity molecules repel each other), then as $W_1 \to \infty$ the $T = T(\eta)$ curve becomes nonmonotonic near the point $\eta = 1/2$, going through a maximum at $\eta = 1/2$. For $\eta = 1/2$, when $W_1 = \infty$, the phase-transition temperature is given by

$$kT(^1/_2)=-V_0/\ln\left(\gamma^2\sum_{k=1}^{\infty}A_{2k}\right). \tag{40}$$

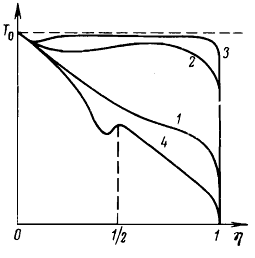

FIG. 2

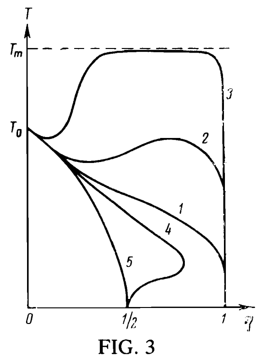

FIG. 3

Comparing (40) with (39) at $\eta = 1/2$, we can easily verify that the temperature $T(1/2)$ is lower at $W_1 = \infty$ than the corresponding temperature at $W_1 = 0$ if

$$\frac{\omega_1}{\omega_2}+\gamma^2\psi(1)>4\gamma^2\sum_{k=1}^{\infty}A_{2k}. \tag{41}$$

In this case the phase-equilibrium curve is given by plot 4 of Fig. 2.

We now proceed to C2, for which the $T = T(\eta)$ relation is given by Eqs. (33) and (34). At $W_1 < 0$ and $|W_1| \to \infty$, the $T = T(\eta)$ curve for $0 < \eta < 1$ tends to a certain straight line $T = T_m$, and deviates from this line only near $\eta = 0$ and $\eta = 1$ (curve 3 of Fig. 3). The value of T_m is determined from (33) and (34) in obvious fashion:

$$\exp\left(-\frac{V_0}{kT_m}\right)=\frac{\omega_1}{\omega_2}+2\gamma^2\psi(1). \tag{42}$$

With a view to the discussion that follows, we introduce the notation

$$y=\frac{\omega_1}{\omega_2}+2\gamma^2\psi(1). \tag{43}$$

It follows from (42) that the limiting phase-transition temperature T_m exists only at $y < 1$. On the other hand, if $y > 1$, then the limiting temperature vanishes. In this case there exists for $|W_1| \to \infty$ an interval of η within which only the double-chain phase is realized at all times. The end points of this interval are determined from (33) by equating the right-hand side of this equation to unity.

We have already noted that at $W_1 > 0$ the $T = T(\eta)$ curve does not go through the point $\eta = 1$ if $W_1 > V_0/2$. In the interval of values $V_0/2 < W_1 < V_0$, Eq. (33) yields a double-valued dependence of the transition temperature on the concentration η for $\eta \geq 1/2$ (curve 4 of Fig. 3), and near the point ($\eta = 1/2$, $T = 0$) the phase-equilibrium curve takes the form (at small $\eta - 1/2$):

$$kT=(-V_0+2W_1)/2\ln(\eta-{}^1/_2), \quad \eta\geqslant{}^1/_2. \tag{44}$$

At $W_1 \geq V_0$ in the interval $1/2 < \eta \leq 1$ the equilibrium phase is always the denatured phase, and for $0 \leq \eta \leq 1/2$ the phase-transition temperature depends uniquely on η (curve 5 of Fig. 3) and takes the following form near the point ($\eta = 1/2$, $T = 0$) at small $|\eta - 1/2|$:

$$kT=-V_0/2\ln({}^1/_2-\eta), \quad \eta\leqslant{}^1/_2. \tag{45}$$

In concluding this section, the following remark is in order. In the discussion of the results we have considered a number of times the approach of the phase-position curves to zero temperature. We are well aware that the real physical system of interest to us is definitely not described by the employed simplified model at sufficiently low temperatures. The analyzed relations, however, enable us to trace the tendency of the restructuring of the phase-equilibrium curves when the parameters of the problem are varied.

4. DEPENDENCE OF THE PHASE-TRANSITION TEMPERATURE ON THE IMPURITY CONCENTRATION IN THE SOLUTION

Primary physical interest attaches to the dependence of the phase-transition temperature not on η but on the impurity concentration of the solution. It is precisely this concentration which can be directly monitored and regulated. Assuming that the impurities on the polymer chain and in the solution are in equilibrium, it is easy in principle to relate η with the concentration of the dissolved matter. If a low-molecular substance forms a weak solution of concentration c ($c \ll 1$), then we have in the solution

$$\mu_1 = kT\ln c + f, \tag{46}$$

where f is a certain smooth function of the temperature.

From the equality of the chemical potential μ_1 on the polymer chain, as given by (29), to the chemical potential in the solution (46), we obtain the connection between η and c:

$$\eta = \frac{1}{2}\left(1 + \frac{ce^{\beta(W_2 - W_1)} - 1}{D}\right), \tag{47}$$

$$W_2 = f + W_0, \quad D = [(ce^{\beta(W_2-W_1)} - 1)^2 + 4ce^{\beta W_2}]^{1/2}.$$

To find the dependence of η on c on the phase-equilibrium curve $T = T(\eta)$ it is necessary to eliminate the temperature T from (47).

We consider first the simplest case $W_1 = 0$, for which the relation $c = c(\eta)$ can always be represented in explicit form:

$$c = \exp\left(-\frac{W_2}{kT_0}\right)\eta(1-\eta)^{(2W_2 - V_0)/V_0}, \tag{48}$$

where T_0 is the phase-transition temperature at $\eta = 0$. It is clear that expressions (47) and (48) are valid only under the condition $c \ll 1$, which was implied in (46).

We assume now that $\exp(-W_2/kT_0) \ll 1$. It follows then from (48) that at $2W_2 > V_0$ the function $\eta = \eta(c)$ is double-valued. Using $\eta = \eta(T)$ from (39), we verify that a phase transition is possible in this case only for $c \le c_m$, where c_m is obtained from formula (48), in which we must put $\eta = \eta_m = V_0/2W_2$. Each concentration c corresponds in this case to two phase-transition temperatures (curve 2 of Fig. 4). If $c > c_m$, the polymer chain is in the split state at any temperature. At $T = 0$, the energywise-favored phase with the split chain elements [4], to each of which an impurity molecule is attached ($\eta = 1$), is always stable. At $2W_2 < V_0$, each c corresponds to a unique value of the phase-transition temperature (a plot of the type 3 in Fig. 4). At $2W_2 = V_0$, the phase-transition curve terminates at the point $c_t = \exp(-W_2/kT_0)$ on the abscissa axis (curve 1 of Fig. 4). At $c < c_t$ there can exist in this case two phases, and at $c > c_t$ only the denatured phase is at equilibrium.

At arbitrary W_1 it is possible to obtain only an implicit relation $T = T(c)$ for the phase-equilibrium curves. Using formulas (12)–(16), (20), (21), (24), (25), and (46), we obtain for C1

$$e^{-\beta V_0} = \frac{\omega_1}{\lambda_2^2} + \frac{\gamma^2}{(1+s^2)^2}\left[s^4\psi\left(\frac{\lambda_1^2}{\lambda_2^2}\right) + 2s^2\psi\left(\frac{\lambda_1}{\lambda_2}\right) + \psi(1)\right], \tag{49}$$

and for C2 [5]

$$e^{-\beta V_0} = \frac{\omega_2}{\lambda_2^2}\left[\exp(-\beta_0 V_0) + \gamma^2\left(\frac{\lambda_2}{\lambda_1}\right)^2\psi\left(\frac{\lambda_1^2}{\lambda_2^2}\right)\right], \tag{50}$$

where $\beta_0 = (kT_0)^{-1}$, while $\lambda_{1,2}$ and s are expressed in terms of the concentration c by means of the formulas

$$\begin{gathered}\lambda_{1,2} = {}^1/_2\,\omega_2^{1/2}\,[ce^{\beta(W_2-W_1)} + 1 \mp D],\\ s = {}^1/_2(ce^{\beta W_2})^{-1/2}[ce^{\beta(W_2-W_1)} - 1 + D].\end{gathered} \tag{51}$$

Let us consider the relation $T = T(c)$ under the assumption that

$$ce^{\beta W_2} \ll 1, \quad ce^{\beta(W_2-W_1)} \ll 1. \tag{52}$$

It is clear that at finite temperatures and at energies W_1 and W_2 there are always concentrations c for which the conditions (52) are satisfied. When (52) is satisfied, in the approximation linear in the concentration, (49) and (50) coincide and yield the following dependence of the transition temperature on the concentration:

$$T(c) = T_0\left[1 - 2c\frac{kT_0}{V_0}\exp\left(\frac{W_2}{kT_0}\right)\right]. \tag{53}$$

We see that the initial course of the curves near the point ($c = 0$, $T = T_0$) is universal, does not depend on the interaction energy W_1 of the attached molecules, and is described by the initial section of the plot in Fig. 4. In the next higher approximation in the concentration, however, the behavior of the $T = T(c)$ curves at small c depends essentially on the sign and magnitude of W_1. In particular, the $T = T(c)$ curves can have a minimum at $c \ll 1$. The corresponding curves are always qualitatively described by plots of the type shown in Figs. 4 and 5 for C1 and C2, respectively. At $W_1 < 0$ and $|W_1| \to \infty$ there is no minimum in the case C1, and in C2 the curve has a minimum at the point $c_{\min} \propto \exp(2W_1/kT_0)$, and begins to increase after this minimum is reached (curve 2 of Fig. 5). The position of the minimum shifts to the left with increasing $|W_1|$. The subsequent course of the $T = T(c)$ curve at $W_1 < 0$ and $|W_1| \to \infty$ depends on the value of y determined by (43). If $y < 1$, then the phase-transition temperature reaches a maximum value T_m determined by (42). On the other hand, if $y > 1$, then $T \to \infty$ when c approaches a certain definite value c_0 at which the right-hand side of (50) becomes equal to unity. A phase transition is impossible at $c < c_0$, and only the denatured phase exists at $c > c_0$.

We now turn to extremely low temperatures ($T \to 0$) and $W_1 \neq 0$. We begin with case C1. From (49), assuming

$$1 \ll ce^{\beta(W_2-W_1)}, \quad W_1 \leqslant 0$$

we obtain

$$kT(c) = \frac{W_2 - W_1 - {}^1/_2 V_0}{|\ln c|}, \quad W_2 - W_1 > {}^1/_2 V_0. \tag{54}$$

On the other hand, if

$$1 \ll ce^{\beta W_2} \ll c^2 e^{2\beta(W_2-W_1)}, \quad W_1 \geqslant 0,$$

then

$$kT(c) = \frac{W_2 - 2W_1 - {}^1/_2 V_0}{|\ln c|}, \quad W_2 - 2W_1 > {}^1/_2 V_0. \tag{55}$$

The functions $T = T(c)$ as given by (54) and (55) can be represented qualitatively by the section of curve 2 of Fig. 4 near the point ($c = 0$, $T = 0$). If $W_2 = W_1 + V_0/2$ at $W_1 \le 0$ or $W_2 = 2W_1 + V_0/2$ at $W_1 \ge 0$, then the phase-equilibrium curve terminates at a certain point c_t on the abscissa axis and is described by a curve of the type 1 of Fig. 4 (c_t is the solution of (49) in which the corresponding values of W_2 and $T \to 0$ are substituted). It can

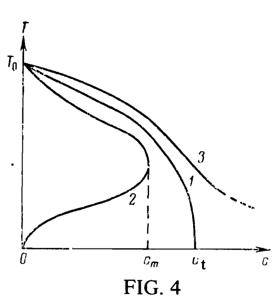

FIG. 4

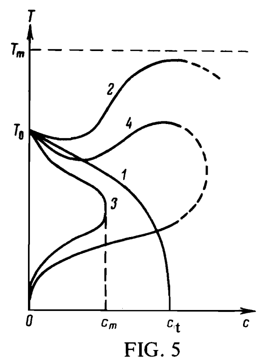

FIG. 5

be verified that when the relations between the parameters differ from those considered here Eq. (49) has no solutions in the region of finite c and at temperatures approaching zero. In this case $T = T(c)$ can always be represented qualitatively by curve 3 of Fig. 4.

Let us consider the case C2. If the inequalities

$$1 \ll ce^{\beta(W_2-2W_1)}, \quad 1 \ll c^2e^{2\beta(W_2-W_1)},$$

hold, then it follows from (50) at $W_1 \le V_0/2$ and $W_2 - W_1 > V_0/2$ that

$$kT(c) = (W_2 - W_1 - {}^1/_2V_0)/|\ln c|. \tag{56}$$

On the other hand, if

$$ce^{\beta(W_2-2W_1)} \ll 1, \quad 1 \ll ce^{\beta W_2},$$

then we obtain at $W_1 \ge V_0/2$ and $W_2 > V_0$

$$kT(c) = (W_2 - V_0)/|\ln c|. \tag{57}$$

The phase-equilibrium curves (56) and (57) are represented by the corresponding section of curve 3 in Fig. 5. If $W_2 = W_1 + V_0/2$ at $W_1 \le V_0/2$ or if $W_2 = V_0$ at $W_1 \ge V_0/2$, then the $T = T(c)$ curve terminates on the abscissa axis at a certain point c_t (curve 1 of Fig. 5), determined from Eq. (50). For C2, a "return" of the phase-equilibrium curve to the origin does not contradict the existence of the minimum for the upper branch of the double-valued relation $T = T(c)$. This case corresponds to curve 4 of Fig. 5.

Thus, double-valued relations $T = T(c)$ are obtained if certain perfectly defined inequalities, which admit of a simple physical interpretation, are satisfied. We shall spell out these qualitative considerations only as applied to C1. As $T \to 0$, the entropy contribution to the thermodynamic potential ceases to play a role, and everything is determined by the extent to which the state is energywise favored. If the ground-state energy E_d of the denatured phase (for complementary pairs of elements) is less than the corresponding energy E_p in the double-chain phase, then the denatured state is realized as $T \to 0$. Taking into account the energy f of the impurity molecule in the solution [Eq. (46)], we can easily verify that for denatured filaments at $W_1 < 0$ there is realized a state in which $\eta = 1$ at $W_2 > W_1$ ($E_d = -2W_2 + 2W_1$) and $\eta = 0$ at $W_2 < W_1$ ($E_d = 2f$). On the other hand, if $W_1 > 0$ then $\eta = 1$ at $W_2 > 2W_1$ and $\eta = 0$ at $W_2 < 0$, whereas in the interval $0 < W_2 < 2W_1$ there is realized the case $\eta = 1/2$ with attached and nonattached impurity molecules of the elements alternating along each filament ($E_d = -W_0 + f$).

In the ground state of C1 at $W_1 < 0$, the double chain does not contain any rings, and therefore $\eta = 0$ and $E_p = -V_0 + 2f$. On the other hand, if $W_1 > 0$, then at $V_0 < 2W_2$ such a state can experience competition on the part of an "altered" chain, along which definite linked and separated pairs with impurity molecules alternate in a strict sequence ($\eta = 1/2$, $E_p = 1/2(-V_0 - 2W_0 + 2f)$). Stipulating now that $E_d < E_p$, we find that as $T \to 0$ and for any positive concentration c there is realized a strictly ordered ($\eta = 1$) denatured structure if $W_2 - W_1 > V_0/2$ at $W_1 \le 0$ or $W_2 - 2W_1 > V_0/2$ at $W_1 \ge 0$. These conditions coincide exactly with the inequalities in (54) and (55).

A similar analysis for C2 leads to the inequalities of (56) and (57).

To reduce the number of parameters, we did not consider changes in the flexibility of the filaments upon attachment of the impurity molecules. It can be verified, however, that allowance for these effects does not qualitatively change the typical forms of the plots of $T = T(\eta)$ and $T = T(c)$. Variation of the flexibility of rings leads to the appearance of a dependence $A_m = A_m(\eta)$, and consequently $A_m(c, T)$, which changes the rate of convergence of the series $\psi(x) = \Sigma A_m x^m$, meaning a change in the form of the phase transition along the phase-equilibrium curve.

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[1] We assume that one outermost pair of elements of the macromolecule is always coupled.

[2] In C2, our results can easily be generalized to include a double chain in which there is no complementarity, and the two filaments of the ring (or tail) can have different lengths. To obtain this generalization it is necessary to replace A_m in the corresponding sums by $(2m - 1) \times A_m$ and to modify somewhat the summation in Z^F. If the series $\Sigma (2m - 1) A_m x^m$ then has properties that ensure the feasibility of a phase transition, then the conditions (24) and (25) remain the same as before.

[3] It is obvious that the corresponding transition is a second-order phase transition.

[4] Of course, the remark made at the end of the preceding section concerning T = 0°K still remains in force.

[5] In the derivation of the relation $T = T(c)$ we did not use the concrete form of the function $\psi(x)$, and the transition in question can be of any order. In addition, the case C2 admits of the possibility that the filaments of the macromolecule are not complementary.

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