Zh. Eksp. Teor. Fiz. 19, 588 (1974) [JETP Lett. 19, 306 (1974)].
[11] R. T. Mina and M. S. Khaĭkin, Zh. Eksp. Teor. Fiz. 48, 111 (1965) [Sov. Phys. JETP 21, 75 (1965)].
[12] P. Laeng and L. Rinderer, Cryogenics 12, 315 (1972).
[13] J. D. Livingston and W. De Sorbo, Superconductivity, ed. Parks, Vol. II, New York, 1969, p. 1240.
[14] F. Haenssler and L. Rinderer, Helv. Phys. Acta 38, 448 (1965).
[15] A. F. Andreev, Pis'ma Zh. Eksp. Teor. Fiz. 4, 7 (1966) [JETP Lett. 4, 4 (1966)].
[16] J. Provost, E. Paumier, and A. Fortini, J. Phys. F 4, 439 (1974).

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# Structure of a polymer globule formed by saturating bonds

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A statistical-thermodynamic analysis is presented of the spatial structure of a long polymer chain in which the loosely-spaced links merge into pairs and form saturated bonds. It is shown that with decreasing temperature such chains form a globular type of structure with irregular joining of the functional links. Although the interaction is by itself incapable of forming a condensed phase, it can lead in a polymer chain to a coil-globule phase transition. The transition is unique in that although formally it is of first order, it is in fact very similar to a second-order transition (the density discontinuity, the heat released, etc. are comparatively small). The extreme cases of a sufficiently short chain in which the excluded monomer volume is of no significance and of an extremely long chain are investigated analytically. A numerical calculation in the intermediate region it has made it possible to fit together the two asymptotic values.

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## 1. INTRODUCTION

The spatial structure of a polymer chain suspended under equilibrium conditions in a dilute solution, is determined by the interactions (direct or via the solvent medium) between the particles of the chain. If these interactions are strong eneough, then they stabilize various structure elements, as a result of which, depending on the concrete character of the acting forces, the polymer coils can turn into globules, helices, folded structures, etc.

The interactions of the parts of the chain with one another and with particles of the solvent are divided into two qualitatively different classes: saturated bonds (covalent, hydrogen) and unsaturated (van der Waals, multipole, etc.). It is known that unsaturated forces lead, with decreasing temperature, to formation of globules of various types. On the other hand, in the case of saturating bonds, the resultant structure depends essentially on the character of the arrangement of the functional (capable of forming bonds) monomers along the chain.

Whereas all the monomers of the chain, or at least those that are densely arranged along it, are capable of forming bonds, a regular conformation of the helical or folded type is thermodynamically not profitable; examples are the $\alpha$ helix or the $\beta$ structure of polypeptides. In essence, the reason why such regular structures are thermodynamically favored is the rigidity of the section of the chain between the neighboring functional groups, as a result of which the entropy loss occurring when a definite conformation is fixed is small.

The opposite case, however, wherein the functional units are quite widely spaced and are separated by flexible pieces of chain, is also possible (the distance between these pieces along the chain is larger than or of the order of the so-called persistence length, i.e., the length over which the memory of the direction is lost). In this situation, any structure with a definite fixed method of binding the pieces of the chain is entropywise unprofitable, so that the chain should (with decreasing temperature) form a structure of the globular type, in which most closed bonds are made up of particles that are very widely spaced along the chain.

This paper is devoted to an analysis of the spatial structure of the globule and of the coil–globule phase transition in such systems.

Under conditions when the functional groups are separated by long sections of a "nonfunctional" chain, it is natural to assume that the length of the bond between two linked ("reacting") groups is small in comparison with the length of the "nonfunctional" section. We can therefore employ the formalism developed in[1] and[2] for a statistical-thermodynamics description of the polymer chain with short-range (in the sense indicated above) forces of lateral interaction. We recall that an essential feature of this formalism was the method of introducing into the theory a concrete form of lateral interaction: all the results were expressed in terms of thermodynamic functions of a gas of broken links with a given interaction. It is natural to take the term link to mean here an entire piece of the chain with one functional monomer. From this point of view, the considered interaction (more accurately, its "attracting" part) in a gas of links reduces to the fact that the "atoms" of this gas can join into "diatomic molecules." The distinguishing feature of the situation is that such interactions cannot cause any phase transition or phase stratisfication at all in a system without linear memory (a gas of links). We shall show, however, that a linear memory changes the situation in the sense that saturating bonds lead to a first-order coil–globule transition, although no phase stratification is obtained in the resultant globule.

The plan of the subsequent exposition is the following: In the second section we consider a very simple model, in which the lateral interaction reduces completely to rare pairwise saturating bonds. If turns out that such a system collapses to dimensions on the order of the length of the link. Therefore it is necessary to supplement the model with allowance for the excluded volume of the links, i.e., the repulsion forces at atmoic distances. This refinement will be introduced in the third section. Finally, Sec. 4 is devoted to a certain generalization to systems with arbitrary interactions of monomers.

Let us recall the fundamental equations previously derived[1–2] for the description of the structure of the globule:

$$\hat{g}\psi=\Lambda\exp\{\mu^*(n)/T\}\psi, \tag{1}$$

$$n=\psi^2\exp\{\mu^*(n)/T\}, \tag{2}$$

$$N=\int n\,d^3r, \tag{3}$$

Here $\hat{g}$ is a linear-memory integral operator, the kernel of which can be naturally regarded under the conditions of the problem as Gaussian, $n(\mathbf{r})$ is the distribution of the density of the number of links, $\Lambda$ and $\psi(\mathbf{r})$ are auxilliary quantities (the function is proportional to the distribution of the density of the end links), $N$ is the total number of links in the chain, $\mu^*=\mu-\mu_{id}$, $\mu(n, T)$ is the chemical potential of the gas of the links, and $\mu_{id}=T\ln n$ (for details see[2]). After solving the equations, the free energy of the globule, reckoned from the free energy of the coil, can be calculated from the formula

$$F=-NT\ln\Lambda-\int p^*\,d^3r, \tag{4}$$

where $p^*=p-p_{id}$, $p$ is the pressure in the system of the broken links, and $p_{id}=nT$.

In this paper we shall not take into account explicitly the influence of the solvent. It is implied that all the employed characteristics of the system are so renormalized that this influence is effectively taken into account. The method of this renormalization was indicated earlier[3]; the singularities to which it leads in this case will be considered in another article.

## 2. CHAIN WITHOUT EXCLUDED VOLUME

Thus, we consider a chain for which the gas of links constitutes a mixture of one- and two-atom ideal gases in the sense indicated above. Let $n_1$ and $n_2$, $\mu_1$ and $\mu_2$ be the partial densities and chemical potentials, respectively, of single-link atoms and two-link molecules, $n=n_1+2n_2$ the total density of the gas of the links; $x=2n_2/n$ is the concentration of the reacting links. The condition for chemical equilibrium is, as is well known,

$$2\mu_1=\mu_2. \tag{5}$$

In the considered case of an ideal gas, the condition reduces to the law of effective masses

$$kn_1^2=n_2, \tag{6}$$

where $k=\exp(-U/T)v_0$ is the binding constant of the link. Here $U$ is the binding energy and $\ln v_0$ is the entropy of the bond; in the classical case $v_0$ is the volume available for the motion of one of two bound particles when the second one is made immobile.

It will be convenient in what follows to rewrite condition (6) in the form of a connection between the equilibrium values of $n$ and $x$:

$$2nk=x/(1-x)^2. \tag{7}$$

It is easy to verify that the volume density of the free energy of the mixture of a monatomic and diatomic ideal gas, reckoned from the density of the free energy of an ideal monatomic gas of nonreacting particles, can be written with the aid of (7) in the form

$$f_0^*=f_0-f_{id}=nT[\ln(1-x)+x/2]. \tag{8}$$

From this we get

$$\mu_0^*=\mu_0-\mu_{id}=\partial f^*/\partial n=T\ln(1-x).$$

This result must be substituted in (1) and (2). We recall that the kernel of the operator $\hat{g}$ is in our case the Gaussian function $g(r)=(4\pi a^2)^{-3/2}\exp\{-r^2/4a^2\}$. For convenience, we introduce a new unknown function $y=[x/(1-x)]^{1/2}=(2n_2/n_1)^{1/2}$ and a dimensionless coordinate $\xi=\mathbf{r}/a$. The complete system of equations then takes the form

$$\hat{g}(y+y^3)=\Lambda y, \tag{9}$$

$$\beta=\int(y^2+y^4)\,d^3\xi,\quad \beta=2Nk/a^3, \tag{10}$$

$$n=(2k)^{-1}(y^2+y^4).$$

The system (9) and (10) contains only one dimensionless parameter $\beta$. It is easiest to solve at large $\beta$. In this case $y$ is large almost everywhere where there are still particles (an estimate is given below), and we can neglect $y$ in comparison with $y^3$, and $y^2$ in comparison with $y^4$. (According to (7), in this approximation we assume almost all the particles to have reacted and almost all the bonds closed.) The resultant simplified equations have a solution in the form of a Gaussian

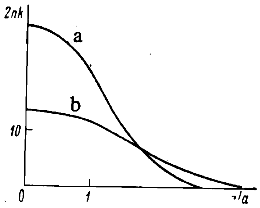

FIG. 1. Density profiles at $\beta = 400$: a—density profile based on formula (11), b—calculated numerically.

function. As a result of some manipulations we obtain for the density profile

$$n(r) = (N/a^3)(2/3\pi)^{3/2}\exp\{-2r^2/3a^2\} \tag{11}$$

and from (4) for the free energy

$$F = (NT/2)[1 - \ln(2/27\pi)^{3/2}\beta]. \tag{12}$$

We call attention to the fact that in this approximation the width of the density profile depends neither on the temperature, nor on the properties of the bonds, nor on the length of the chain.

It is now necessary to use the results to find the region of its applicability: it is necessary to stipulate smallness of the fraction of the links that are situated outside of a radius $R$ such that $kn(R) \sim 1$. A numerical analysis leads to the estimate

$$\beta = 2Nk/a^3 \gg 1000. \tag{13}$$

Contributing to the satisfaction of this condition are lowering of the temperature, the strength of the bonds, and the length and flexibility of the chain.

However, condition (13) is violated before the globule is transformed into a coil (according to (12), this transition should take place at $F = 0$, i.e., $\beta = e(27\pi/2)^{3/2} \approx 750$). It is therefore necessary to carry out an analysis of the system of equations (9) and (10) in the region where it does not contain a small parameter. The results of this analysis, carried out with a BÉSM-4M computer, are considered in the Appendix; here, we report only those results which are needed for our purposes. At $\beta = 6000$, the obtained density profile coincided with the analytical results (11) within less than 10%. With decreasing $\beta$, the density profile smears out noticeably and ceases to be Gaussian. By way of example, Fig. 1 shows the profile of $n(r)$ at $\beta = 400$.

Calculating the free energy from the numerically obtained density profiles, we find that the globule–coil phase transition takes place at

$$\beta = \beta_1 \approx 195 \tag{14}$$

and is a first-order transition. At the transition point, the radius at which the density amounts to $0.1\, n(0)$ is approximately 3.4 times larger than (11).

Thus, a chain without an excluded volume with loosely-spaced saturating bonds forms under suitable conditions (low temperature, strong bonds, long and flexible chain $\beta > 195$) a globule whose dimension depends little on the temperature and on the length of the chain and remains of the order of the length $a$ of one link.

The quantity $a$ was introduced above as the dispersion of the Gaussian kernel. This form of the kernel $\hat{g}$ is natural, but in the general case not at all mandatory (the results of the present study are not very sensitive to the actual form of the nucleus). However, the quantity $a$ can be introduced also in the general case as the mean spatial distance between two functional monomers that are neighbors along the chain. This quantity is connected with the distance $l$ between them along the chain and with the persistence length $l_0$ by the formula $a^2 = ll_0/3$.

In a real situation there are always repulsion forces at atomic distances, i.e., each link carries an excluded volume $v$. Therefore the results are applicable only under the condition $nv \ll 1$, or (see (11)) $Nv/a^3 \ll 10$[1)] (in terms of the lengths $l$ and $l_0$, this condition takes the form $1 \ll N \ll (l/l_0)^{1/2}$). Consequently, for sufficiently long chains it is necessary to take into account the excluded volume.

## 3. CHAIN WITH EXCLUDED VOLUME

In the presence of an excluded volume, the gas of broken links is no longer a mixture of ideal gases. It is necessary to find the free energy of a gas of particles, each of which is a filament with a finite self-volume (in accordance with the definition of the link). This can be done only approximately, although the qualitative results obtained below are little sensitive in their character to the actual method used to introduce the excluded volume.

We introduce, for example, an excluded volume in analogy with the manner used to introduce it in the van der Waals model. We note first that since in our chain only one monomer from each long link enters into a bond, the volume of the pair of links remains practically unchanged by the bonding. Consequently the second virial coefficients of the interaction of two single links, of a single link and a bound pair of links, or of two pairs are related like 1 : 2 : 4, i.e., they are equal to $v$, $2v$, and $4v$. Using the same reasoning as in[4] in the derivation of the van der Waals equation (but neglecting the van der Waals attraction), we obtain

$$f^* = f_0^* - Tn\ln(1 - nv) = Tn\left[\ln(1 - x) + \frac{x}{2} - \ln(1 - nv)\right], \tag{15}$$

where $f_0^*$ is defined in (8). In this approximation, the chemical-equilibrium condition (5) leads as before to (6) and (7).

We consider first the case of a very long chain, when the dimension of the resultant globule is larger than $a$. In this case, as already shown (see[2]), if $\Lambda$ is not close to unity, the globule contains a coil with a practically constant density $n_0$; around the core, the density decreases rapidly to zero at a distance $\sim a$. The density $n_0$ is determined by the condition $p^*(n_0) = 0$. By determining $p^*$ from (15)

$$\left(p^* = n^2 \frac{\partial}{\partial n}\left(\frac{f^*}{n}\right)\right),$$

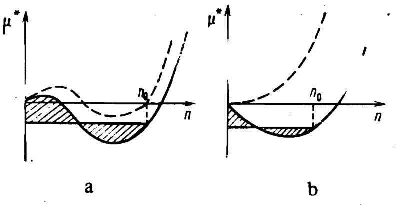

FIG. 2. Plots of $\mu^*(n)$ at constant $T$: a) plot given in[1]; b) plot of formula (18). The dashed lines are the plots of $\mu^*(n)$ at $T = T_c$. In (a) $n_0$ is finite and in (b) $n_0 \to 0$ as $T \to T_c$.

we obtain with the aid of (7)

$$x_0 = {}^1\!/_2[2+\alpha-(\alpha^2+12\alpha)^{1/2}], \quad \alpha = v/2k.$$

From this we get the free energy in the volume approximation (see[2])

$$F = NT\frac{f^*(n_0)}{n_0} = NT\left[\frac{x_0}{2}+\ln(1-x_0)\left(1+\frac{x_0}{2}\right)\right].$$

Let us analyze the coil–globule transition in a long chain. To this end we consider a plot of the function $\mu^*(n) = \partial f^*/\partial n$, shown in Fig. 2. As already indicated (see[1]), the point $n_0$ is determined from the condition that the shaded areas be equal, and the transition temperature is determined from the condition that the horizontal secant coincide with the abscissa axis. It is clear that a first-order transition can be obtained in the volume approximation only when the function $\mu^*(n)$ retains a minimum at large $n$, even above the inversion temperature of the second virial coefficient (the Flory $\Theta$ point), i.e., when at small $n$ we have $\mu^*(n) > 0$, as shown in Fig. 2a. The origin of this minimum is closely connected with the possibility of phase stratification in the gas of links. In the case of (15), however, such a stratification is impossible and the minimum vanishes at the $\Theta$ point. Consequently, no first-order transition is obtained in the volume approximation and when the transition point is approached the density in the globule tends to zero.

To analyze the transition, we can therefore expand $f^*(n)$ in powers of $n$ (the virial expansion)

$$f^*(n) = n^2TB(T)+n^3TC(T),$$
$$B = v-k, \quad C = v^2/2+2k^2.$$

For $f^*$ in this form it is easy to carry out all the calculations of the volume approximation and obtain $n_0 = -B/2C$, $\Lambda = 1+B^2/4C$, and for the free energy $F_v = -NTB^2/4C$. From this we see that the transition point in the volume approximation (i.e., the point where $F_v = 0$) is simply the Flory $\Theta$ point. From the expressions for $n_0$ and $F_v$ it is seen that in this approximation the transition is of second order, without a jump of the density and a gradual spreading of the system. However, besides this spreading, the surface layer becomes thicker, since the width of the surface layer has a characteristic dimension $\sim a/(\Lambda-1)^{1/2}$, and as $T \to T_c$ we have $\Lambda \to 1$. When the transition layer becomes thicker, the surface contribution to the free energy begins to compete with the volume contribution, i.e., the volume approximation no longer holds. It is obvious that both contributions will be of the same order when the thickness of the surface $a/(\Lambda-1)^{1/2}$ is of the order of the globule radius $(N/n_0)^{1/3}$.2) Using $n_0$ and $\Lambda$ obtained in the volume approximation, and recognizing that near the $\Theta$ point we have

$$B(T) \approx b(\Theta)[1-T/\Theta], \quad C(T) \approx C(\Theta),$$

we obtain an estimate for the transition temperature $T_c$:

$$1-T_c/\Theta \sim a^{3/2}C^{1/4}/bN^{1/2}. \tag{16}$$

In our concrete case it is easy to find that $C = (\frac{5}{2})v^2$ and $b = vU/\Theta$, so that

$$1-T_c/\Theta = \mathrm{const}\,(\Theta/U)\,(a^3/Nv)^{1/2}. \tag{16a}$$

The asymptotic formula (16a) holds only for large $N$, when $nv \ll 1$ at the transition point. At intermediate $N$ it is necessary to solve the general system (1)–(4) and obtain $\mu^*$ from (15). A numerical solution for a Gaussian curve was obtained with the BÉSM-4M computer. The obtained first-order phase transition is shown in Fig. 3 in terms of the variables $\alpha$ and $Nv/a^3$. At small $N$ (up to $Nv/a^3 \sim 10$) this curve duplicates the result (14) within 10%. At extremely large $N$, the curve takes the asymptotic form (16a) with const = 6.7. In the interval $0.15 < \alpha < 0.5$ the calculated curve can be approximated within 1% by the expression

$$\frac{1}{2}-\alpha = \frac{6.7}{(Nv/a^3)^{1/2}+10.4}.$$

The average density in the globule at the transition point at large $N$ is small: $\langle nv\rangle_g \sim (a^3/Nv)^{1/2}$. We consider the case $v/a^3 \ll 1$.3) Then the density of the coil4) is $n_c \sim 1/a^3N^{1/2}$, and thus the relative density jump is

$$\frac{n_g-n_c}{n_c} \sim \left(\frac{a_3}{v}\right)^{3/2}.$$

Consequently in this case the coil–globule transition is formally of first order and at large $N$ takes place not much lower than the $\Theta$ point. However, with respect to some of its characteristics, the transition is close to second order. This manifests itself in the fact that, first, the heat of the transition per particle $\Delta Q/N \sim U(a^3/Nv)^{1/2}$ tends to zero as $N \to \infty$. Second, the relative

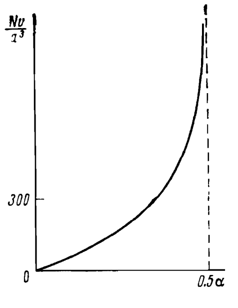

FIG. 3. Phase diagram.

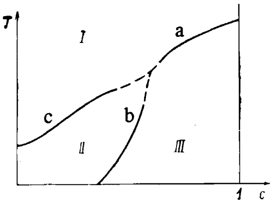

FIG. 4. Phase diagram in terms of the variables ($c$, $T$). I—coil; II—globule; III—helix.

density jump $\sim (a^3/v)^{3/2}$ does not depend on the length of the chain and is small in comparison with the relative jump in the ordinary first-order transition in a system with linear memory $\sim a^3N^{1/2}/v$. Third, the jumplike change of the density in the transition is preceded by a stage of gradual decrease of the average density in the globule to a very small value.

In a finite chain, the coil–globule transition is in fact not a true phase transition but a more or less abrupt cooperative transition of width $\Delta T$. Let us estimate $\Delta T$. The smoothing of the phase transition takes place in an interval in which the difference of the free energies of the phases is $F \sim T \ll NT$ and the equations used by us are not valid. From the estimate given above we easily obtain

$$\Delta T \sim (\Theta - T_c) v/a^3. \tag{17}$$

Thus, in the considered case ($v \ll a^3$) the width of the transition is much smaller than the smallest characteristic temperature interval of the problem $\Theta - T_c$; the transition is close to a first-order phase transition and takes place somewhat below the $\Theta$ point (see 16a).

We consider now the case $v \sim a^3$. It is then seen from (17) that the transition broadens up to the $\Theta$ point, its width turns out to be $\sim N^{-1/2}$, and it must be assumed in practice that even at finite $N$ we are dealing with a transition that occurs at the $\Theta$ point itself. This is not a first-order phase transition in the sense that the distribution function of the system is not "transferred" from the regions of configuration space with large (globule) densities into regions with small (coil) densities, but this probability changes rather continuously.

In concluding this section, let us consider qualitatively the phase diagram of a sufficiently long polymer chain in terms of the variables ($c$, $T$) where $c$ is the concentration of the functional links. For the sake of argument we shall construct the same diagram for the polynucleotide chain poly-AT (which can wind itself around into a helix, forming a "spindle" diluted by nonfunctional links (for example, Γ). At a small concentration of Γ, the chain will preserve in the main the helical structure with defects due to the presence of Γ. The temperature of the helix–coil transition will decrease with increasing concentration of Γ (Fig. 4, curve a). On the other hand, if the concentration of Γ is large enough, then the helical structure is less favored than the globule structure (see Sec. 1), and consequently at a certain concentration a first-order helix–globule transition takes place (curve b of Fig. 4). The obtained globule was investigated above, at a corresponding coil–globule transition is shown by curve c of Fig. 4. At very low concentrations of the functional links, at the coil–globule transition temperature, the most essential role in the attraction of the monomers is played by the unsaturated forces, as a result of which the transition ceases to be described by the formulas of this section, and in the presence of sufficiently strong van der Waals interactions it can proceed as an ordinary first-order phase transition in a system with linear memory (see[2]).

## 4. SOME GENERALIZATIONS

Comparing the conclusions of the present paper with those of[1] and[2], we readily see the large difference between the structures and properties of globules made up of saturated bonds and unsaturated short-range forces. In the case of saturating bonds there are no such phenomena as the appearance of a small globule (with dimensions smaller than the length of link $a$), formation of a sharp boundary between the coil of the globule and its fringe, or the vanishing of the fringe. All these singularities are due to the fact that the saturating bonds with unity valence do not form a condensed phase in the gas of the links. Also closely connected with this fact is, as we have seen, the closeness of the coil–globule transition to a second-order transition.

It is clear that other polymers can behave in similar fashion—the important factor is that the volume interaction lead to a function $\mu^*(n, T)$ of the same type as shown in Fig. 3b. The connection between this property and the phase stratification in a gas of links is clear from the fact that the latter is equivalent to a nonmonotonic behavior of the chemical potential $\mu(n) = \mu^*(n) + T\ln n$. An analysis of the coil–globule transition for such polymers does not differ from that given in Sec. 3—in the general case all that changes is the interpretation of the meaning of the virial coefficients $B$ and $C$.

The role of the parameter analogous to $v/a^3$ in Sec. 3 is played in this case by $C^{1/2}/a^3$. It is seen therefore, first, that the abruptness of the transition will be most clearly pronounced in a solvent in which the third virial coefficient has the smallest possible value. Second, the abruptness of the transition is aided by the increased rigidity of the chain (increase of $a$). These properties of the coil–globule transition below the $\Theta$ temperature agree with the results obtained by others[5–6] by modifying the elementary Flory model and are confirmed by computer simulation.[7–9]

On the other hand, if $\mu^*(n, T)$ takes the form shown in Fig. 3a (this can occur only when the principal role in the the attraction of the links at large densities is played by unsaturating forces), then the coil–globule transition proceeds like the ordinary first-order transition described in the earlier papers.[1–2] The temperature of this transition lies above the $\Theta$ point, and its qualitative characteristics do not depend essentially on the properties of the elementary link.

It is interesting to note that the loosening of the globule prior to the transition into a coil below the $\Theta$ point is in clear qualitative correspondence with the well-known fact[10] that even the most concentrated phase is extra-

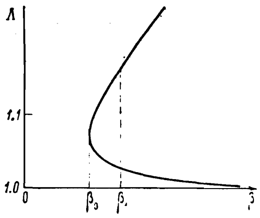

FIG. 5. Plot of $\Lambda(\beta)$, $\beta_0 \approx 145$, $\beta_1 \approx 195$.

ordinarily diluted when a solution of chains is stratified at the Θ point.

We indicate in conclusion that to observe experimentally an abrupt coil–globule transition below the Θ temperature it is necessary that the solution be sufficiently dilute: the chain density $n_g$ in the solution must be so small that the transition into the globule occurs prior to the precipitation of the polymer. To this end it is necessary that the gain in the surface energy when two globules stick together be smaller than the loss of the entropy due to the loss of the degrees of freedom of the relative motion of the globules. An order-of-magnitude estimate leads to the result

$$|\ln n_{\text{г}} v_{\text{г}}| \lessdot a^3 C^{-1/3},$$

where $v_g$ is the volume of the globule.

## APPENDIX

The results of an analysis of the system of equations (9)–(10). The system (9)–(10) specifies $y(\xi)$ and $\Lambda$ as functions of $\beta$. A plot of the function $\Lambda(\beta)$ is shown in Fig. 5. At $\beta < \beta_0 \approx 145$ the system has no nontrivial solutions. At $\beta > \beta_0$ the system has two nontrivial solutions; one of them corresponds to the maximum of the free energy (the solution corresponding to smaller $\Lambda$), and the other to a minimum. At $\beta > \beta_1 \approx 195$ this minimum is absolute and corresponds to the equilibrium state of the system. At $\beta_0 < \beta < \beta_1$ the maximum is local and determines a metastable state, while the equilibrium state is the one corresponding to the trivial solution $y \equiv 0$ (coil). From this point of view, the value $\beta = \beta_0$ is the stability limit of the metastable state.

$y(\xi)$ as a function $\Lambda$ has a monotonic behavior: when the point $\Lambda = 1$ is approached from above, this function "spreads out" and becomes $\ll 1$. In this case we can replace the integral operator $\hat{g}$ by the differential operator $1 + a^2\Delta$, using the fact that $y \ll 1$, and obtain the function $\Lambda(\beta)$, apart from a numberical factor. It turned out that $\beta \sim (\Lambda - 1)^{-1/2}$, and that the solution obtained in this manner is valid at $\Lambda - 1 \ll 1$, i.e., it describes the lower part of curve on Fig. 5, corresponding to the maximum of $F$. Both the transition point and the stability limit of the metastable phase lie at larger values of $\Lambda$.

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[1)] Consequently, in order to be able to neglect the excluded volume at the transition point (14), it is necessary to satisfy the inequality $\alpha \equiv v/2k \ll 0.05$. In order for a region of applicability of the Gaussian approximation (13) to exist, the stronger condition $\alpha \ll 0.01$ is necessary.

[2)] Using the fact that in the transition region the density in the globule is small, and that the density profile changes smoothly, we can write down the equations (1) and (2) in the form $\alpha^2\Delta\psi = (\Lambda - 1)\psi + 2B\psi^2 + 3C\psi^5$, $n = \psi^2$. All the remaining terms of the equation for $\psi$ turn out to be in the region of the first-order transition, owing to the anomalously low value of the coefficient $B$ near the Θ point.

[3)] This case is realized, for example, when the link, having a length on the order of the persistence length, consists of a large number $M$ of monomer groups with identical excluded volume. Then estimates show that $v/a^3 \sim M^{-1} \ll 1$.

[4)] At the transition temperature, the parameter of the volume interaction in the coil is $N^{1/2}B/a^3 \sim (v/a^3)^{1/2} \ll 1$, i.e., the coil can be regarded as Gaussian.

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[1] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **55**, 2408 (1968) [Sov. Phys. JETP **28**, 1280 (1969)].
[2] I. M. Lifshitz and A. Yu. Grosberg, Zh. Eksp. Teor. Fiz. **65**, 2399 (1973) [Sov. Phys. JETP **38**, 1198 (1974)].
[3] I. M. Lifshitz and A. Yu. Grosberg, Dokl. Akad. Nauk SSSR **220**, 468 (1975).
[4] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964; [Pergamon 1971].
[5] Yu. E. Eĭzner, Vysokomol. Soed. **A11**, 369 (1969).
[6] P. G. de Gennes, J. Phys. Lett. **36**, 55 (1975).
[7] A. K. Kron, O. B. Ptitsyn, A. M. Skvortsov, and A. K. Fedorov, Mol. Biol. (Moscow) 1, 576 (1967).
[8] A. M. El'yashevich and A. M. Skvortsov, Mol. Biol. (Moscow) 5, 204 (1971).
[9] T. M. Sirshtein, A. M. Elyashevich, and L. A. Morgenstern, Biophys. Chem. 1, 242 (1974).
[10] P. Flory, Principles of polymer chemistry, 1953, New York, Ch. 12.

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