Phase diagram of two-component polymer systems and its application to polymer complexes

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A dilute solution of two types of homopolymer chains in the presence of attraction between monomers of different types is considered. It is shown that, for a diblockcopolymer molecule formed by two long chains of different species, the globular state arises in the presence of an arbitrarily weak attraction between monomers of different species, irrespective of the strength of the repulsion between identical monomers. The resulting globule may be surrounded by a coil phase envelope. The density and composition of the globule are found. The equation of state of a dilute two-component solution of long chains are found with the aid of phase transition theory methods. Such a solution stratifies, the denser phase (condensate) being a semidilute solution. The compositions and densities of the two phases are found. It is shown that a long chain of one species in a dilute solution of chains of the other species forms a globule.

INTRODUCTION

Two-component polymers constitute the simplest case of multicomponent systems that allows us to study the characteristic properties of these systems. This is extremely important, since the majority of natural and practically important polymer systems are mixtures or solutions of different polymers. And if for concentrated multicomponent systems there exists fairly well developed methods of investigation and fairly extensive literature (see, for example, Ref. 1), the investigation of dilute and semidilute multicomponent solutions is essentially only beginning. In Refs. 2 and 3 the behavior of the individual molecules is investigated, and in Refs. 4 and 5 the occurrence of flutuation-induced first-order phase transitions in two-component solutions is demonstrated.

In the present paper we consider the following system: long poly-*A* and poly-*B* chains, the solvent being, for each species taken separately, the good polymer. We shall limit ourselves to the low-concentration region, where the decisive role is played by fluctuations and the correlation length is large. The computation of the characteristics of such a system reduces to the problem, well known in the theory of phase transitions, of a system with two order parameters, of which at least one undergoes strong fluctuations.[6] It is well known that such a system undergoes fluctuation-induced first-order phase transitions—effects which are absent in the mean-field theories. The specific computations in the present paper are carried out on the basis of this analogy with the aid of the methods of field theory, but the physical meaning of the results obtained can be elucidated with the aid of simple arguments.

For the two-component system in question we obtain the following results. In §1 we show that, in the presence of an arbitrarily weak attraction between the monomers *A* and *B*, a sufficiently long molecule of the diblockcopolymer $A_N B_M$ will form a globule with a coil-phase "trimming." The density and composition of the globule nucleus depends weakly on N/M, if N and M are sufficiently large.

In §2 we consider a two-component solution of the polymers A_N and B_M. It is shown that arbitrarily weak attraction between the monomers *A* and *B* (even in the presence of strong repulsion between identical monomers) leads to the appearance of a region of phase stratification on the phase diagram of the solution. The lighter phase is a dilute solution occurring far from the stratification critical point, while the denser phase (which we call the condensate, since it should separate out as a precipitate) is a semidilute solution whose composition depends weakly on the composition of the entire system. It is also shown that in this case a sufficiently long B_M molecule in a dilute A_N solution should form a globule. The "coil→globule" transition is a sharp first order transition. When the concentration of the solution is increased, the inverse transition "globule→coil," which is also of first order, occurs. If the number of B_M molecules in the solution is small, then their transition into the globular state will not lead to precipitation, but will give rise to turbidity of the solution. When the density of the globules in the solution increases, their attraction will lead to the formation of a condensate.

The main idea of the computations is as follows. As is the case for any solution of low concentration, the system under investigation is entirely determined by the second virial coefficients B_{AA}, B_{AB}, and B_{BB} for the *A*–*A*, *A*–*B*, and *B*–*B* interactions, as renormalized by the interaction with the solvent and the nearest—according to the quasimonomer concept[7]—neighbors along the chain. We must compute for the case in which $B_{AA}, B_{BB} > 0$ and $B_{AB} < 0$ the free energy $F(\rho_A, \rho_B)$ of a unit volume of a solution of infinitely long poly-*A* and poly-*B* chains with prescribed mean densities ρ_A and ρ_B, as measured from the free energy of the coil state of these same chains. It is precisely this quantity that enters into the equations of the globule theory developed by I. M. Lifshitz (see Ref. 8 for a review), and determines the state of the macromolecule $A_N B_M$, as well as the interaction between sufficiently long A_N and B_M molecules. In the Flory theory

$$F(\rho_A, \rho_B) = B_{AA}\rho_A^2 + B_{BB}\rho_B^2 + 2B_{AB}\rho_A\rho_B.$$

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The correlation between the density fluctuations leads to a situation in which we actually have in the case when $B_{AB} = 0$ the estimate

$$F(\rho_A, \rho_B) \sim \rho_A^{9/4} B_{AA}^{-3/4} + \rho_B^{9/4} B_{BB}^{-3/4}.$$

If we treat the attraction between the monomers A and B as a weak perturbation that does not distort the system,[1)] then

$$F(\rho_A, \rho_B) \sim \rho_A^{9/4} B_{AA}^{-3/4} + \rho_B^{9/4} B_{BB}^{-3/4} + 2B_{AB}\rho_A\rho_B.$$

It can be seen from this that, at sufficiently low ρ_A and ρ_B values, the energy $F(\rho_A, \rho_B) < 0$, and the pressure vanishes. Furthermore, the ρ_A-ρ_B correlations lead to the result that in fact $F(\rho_A, \rho_B)$ is smaller than the above-presented estimate. This is a manifestation of a general rule, according to which the true free energy is always smaller than the value computed on the basis of the Flory theory. From this it follows that all the effects described above—the globulization of the molecule $A_N B_M$, the stratification of the semi-dilute solution as a result of the negativeness of the pressure at very low values of ρ_A and ρ_B, etc.—will occur under conditions of arbitrarily small $B_{AB} < 0$.

The reason why a weak attraction between the monomers A and B has such a strong effect on the behavior of the entire system is that the nature of the interaction between attractive polymer chains is entirely different from that of the interaction between repulsive ones. As two repulsive chains, e.g., A and B, approach each other, the interacting monomers tend to separate, and, in so doing, push apart their nearest neighbors along the chain, thereby inhibiting their interaction. This leads to the well-known screening of the interaction: the mean interaction energy of such chains remains constant as their length is increased.[9] If, on the other hand, the chains attract each other, then the interacting monomers approach each other and draw their neighbors along the chain together, thereby intensifying their interaction. As a result, instead of screening, there occurs intensification of the interaction: the energy of long attractive chains is greater (in absolute value) than the estimate given by the Flory theory, and tends to $-\infty$ as the length of the chains increases.

§1. CONFORMATION OF A LONG DIBLOCKPOLYMER IN A SOLUTION

Let us consider an isolated long (N and M are large) $A_N B_M$ molecule in the $B_{AB} < 0$ case of interest to us. We shall consider the quantity $p_0^2 = B_{AB}^2/(B_{AA}B_{BB})$ to be small: we can investigate the phase-state diagram in this case. The state of such a model is entirely determined[8] by the free-energy density $F(\rho_A, \rho_B)$ introduced above.[2)] We shall give here a simplified estimate for it; a more exact calculation is presented in the Appendix.

Let in the solution of infinitely long chains that is being considered by us the mean distance between the linkages (or, which is the same in the present case, the correlation length) be equal to R_c. This scale can, in principle, have different values for the poly-A and poly-B chains, but, as will be shown below, this does not occur. If we carry out the $F(\rho_A, \rho_B)$ computation in terms of the original A and B monomers, then we are faced with the necessity of the consideration of the long-range correlations. In the low-density case of interest to us R_c is large, and the correlation effects make, as has already been indicated, the dominant contribution. Therefore, we shall go over to new monomers consisting of $\mathcal{N}_A(R)$ A monomers in the case of the poly-A chains and $\mathcal{N}_B(R)$ B monomers in the case of the poly-B chains, and having geometrical dimensions equal to[3)] R:

$$\mathcal{N}_A(R) \sim R^{5/3}(B_{AA}l_1^2)^{-1/3}, \qquad \mathcal{N}_B(R) \sim R^{5/3}(B_{BB}l_2^2)^{-1/3},$$

where l_1 and l_2 are the persistent poly-A and poly-B chain lengths. If we choose $R = R_c$, then we find that the condition of applicability of the mean-field theory is fulfilled: the correlation length is of the order of the monomer size. Therefore, we could have written the virial expansion for $F(\rho_A, \rho_B)$ in terms of the densities η_A and η_B of the new monomers:

$$\eta_A = \rho_A/\mathcal{N}_A(R_c), \qquad \eta_B = \rho_B/\mathcal{N}_B(R_c).$$

Since the density dependence of R_c is known:

$$R_c \sim \eta^{-1/3} \sim \rho^{-3/4} B^{-1/4} l^{-1/2},$$

to obtain the final expression for $F(\rho_A, \rho_B)$, we need only determine the virial coefficients for the new monomers. Such calculations are carried out in Ref. 4, and we briefly report here the main conclusions and results.

The system under investigation can be compared to a two-field model with the Hamiltonian

$$\begin{gathered}
H(\varphi_{1\alpha}, \varphi_{2\alpha}) = \int \{ {}^1/_2 [\tau_1\varphi_1^2(\mathbf{x}) + \tau_2\varphi_2^2(\mathbf{x}) + (\nabla\varphi_1(\mathbf{x}))^2 \\
+ (\nabla\varphi_2(\mathbf{x}))^2] \\
+ g_{11}(\varphi_1^2(\mathbf{x}))^2 + g_{22}(\varphi_2^2(\mathbf{x}))^2 + 2g_{12}\varphi_1^2(\mathbf{x})\varphi_2^2(\mathbf{x}) \} d^d\mathbf{x}, \\
\varphi^2 = \sum_\alpha \varphi_\alpha^2, \qquad (\nabla\varphi)^2 = \sum_\alpha (\nabla\varphi_\alpha)^2, \\
g_{11} = B_{AA}/8l_1^4, \qquad g_{22} = B_{BB}/8l_2^4, \qquad g_{12} = B_{AB}/8l_1^2l_2^2,
\end{gathered} \tag{1.1}$$

and $\varphi_{1\alpha}$ and $\varphi_{2\alpha}$ are n-component fields, with $n \to 0$. The dimensionality of the space is equal to d. Let us, for simplicity, set the temperature T equal to unity; then the model free energy (1.1) is the thermodynamic potential

$$\Omega(\rho_A, \rho_B) = F(\rho_A, \rho_B) - \mu_A\rho_A - \mu_B\rho_B$$

of the above-described solution of infinitely long chains (we have dropped the volume factor, which is insignificant here). In this expression

$$\begin{gathered}
\mu_A = -\tau_1 l_1^2, \qquad \mu_B = -\tau_2 l_2^2, \\
\rho_A = {}^1/_2 l_1^{-2}\langle\varphi_1^2(\mathbf{x})\rangle, \qquad \rho_B = {}^1/_2 l_2^{-2}\langle\varphi_2^2(\mathbf{x})\rangle.
\end{gathered} \tag{1.2}$$

The second virial coefficients $B_{AA}^R(R)$, $B_{BB}^R(R)$, and $B_{AB}^R(R)$ for the interaction between the new monomers can be expressed in terms of $\Gamma_{11}(R)$, $\Gamma_{22}(R)$, and $\Gamma_{12}(R)$, the sums of the irreducible four-point diagrams of the model (1.1), in which the external momenta are of the order of $1/R$:

$$B_{AA}{}^{R}(R)\sim 8\Gamma_{11}(R)R^{4},\qquad B_{BB}{}^{R}(R)\sim 8\Gamma_{22}(R)R^{4},$$
$$B_{AB}{}^{R}(R)\sim 8\Gamma_{12}(R)R^{4}. \tag{1.3}$$

The vertex functions $\Gamma_{ik}(R)$ are computed in Ref. 6 in the first approximation in $\varepsilon = 4 - d$:

$$\Gamma_{11}=g_{11}(1+32g_{11}\xi)^{-1},\qquad \Gamma_{22}=g_{22}(1+32g_{22}\xi)^{-1},$$
$$\Gamma_{12}=g_{12}\left[16g_{12}f(\xi)\int\limits_{0}^{\xi}\frac{dx}{f(x)}+f(\xi)\right]^{-1}, \tag{1.4}$$
$$f(\xi)=[(32g_{11}\xi+1)(32g_{22}\xi+1)]^{1/4},\qquad \xi=\left(\frac{R^{\varepsilon}}{a^{\varepsilon}}-1\right)(4\pi^{2}\varepsilon)^{-1},$$

here a is the (atomic) dimension of the A or B monomer. It can be seen from (1.3) and (1.4) that $B^{R}_{AB}(R)$ has a pole at a finite value of R. The solution (1.4) is not valid in the vicinity of the pole, but the stability condition for the homogeneous state, $(B^{R}_{AB}(R))^{2}\leqslant B^{R}_{AA}(R)B^{R}_{BB}(R)$, is violated in the region of applicability of (1.4).

The higher virial coefficients are proportional to the sixth- and higher-order vertex functions, and therefore tend rapidly to zero with increasing R. This result is exact.[10]

Our subsequent field-theoretic calculations are also carried out in the first ε approximation (see the Appendix), but in a number of cases the sought dependence can be determined with the use of the usual scaling arguments. In these cases we shall immediately substitute the critical exponents for three-dimensional space. But if we cannot do this, then we shall retain the symbol ε in such relations, and only in the final answer should we set $\varepsilon = 1$.

For simplicity, we shall set the atomic dimension a equal to unity. The virial expansion then has the form

$$F(\rho_{A},\ \rho_{B})\approx B_{AA}{}^{R}(R_{c})\eta_{A}{}^{2}+B_{BB}{}^{R}(R_{c})\eta_{B}{}^{2}+2B_{AB}{}^{R}(R_{c})\eta_{A}\eta_{B}.$$

As is well known,[9] at large R values $B^{R}(R)/R^{d}\to\lambda$, where the constant λ depends only on the dimensionality of the space, and we can assume that

$$B_{AA}{}^{R}(R_{c})=B_{BB}{}^{R}(R_{c})=B^{R}(R_{c})\sim\lambda R_{c}{}^{d}.$$

The preceding formula can in this case be rewritten in the form

$$F(\rho_{A},\ \rho_{B})\approx B^{R}(R_{c})\,[(\eta_{A}-\eta_{B})^{2}+2y\eta_{A}\eta_{B}],$$
$$y=B_{AB}{}^{R}(R_{c})/B^{R}(R_{c})+1. \tag{1.5}$$

From this it can be seen that, firstly, the formation of a globule is thermodynamically advantageous when $y<0$ and, secondly, the composition of the globule is quite strictly fixed by the first term in (1.5). The composition of the globule turns out to be precisely such that one and the same R_c value is obtained for both the A and B monomers.

But the situation of the formula (1.3) into (1.5) yields a totally incorrect value for the coefficient of $\eta_A\eta_B$. A more exact calculation carried out in the Appendix in the first ($\varepsilon = 4 - d$)- approximation yields the following expressions for the thermodynamic functions:

$$P=-\Omega/V=(64\pi^{2})^{-1}(1-x^{-1})R_{c}^{-d}+(\eta_{A}^{1/2}-\eta_{B}^{1/2})^{2}/2, \tag{1.6}$$
$$F=-(64\pi^{2})^{-1}(1+x^{-1})R_{c}^{-d}+(\eta_{A}^{1/2}-\eta_{B}^{1/2})^{2}/2.$$

Here x is a dimensionless parameter that can be determined implicitly in terms of R_c and assumes values ranging from $\frac{1}{2}(\varepsilon/8)^{\varepsilon/2}$ to $+\infty$ for $-\infty<y<y_0$. All the correlators with scale smaller than R_c do not differ from the corresponding correlators for a coil.

Now we can determine in the volume approximation all the characteristics of the globule formed by the diblockpolymer A_NB_M. The globule density is determined by the condition for $F(\rho_A,\rho_B)$ to possess a minimum upon the fulfillment of certain conditions imposed on ρ_A and ρ_B. Here we can have different cases determined by the relation between N and M. If the entire molecule can be packed into a globule nucleus in which $\eta_A = \eta_B$, then its density is given by the condition $P = 0$. Such a situation arises when the following relation is satisfied:

$$N/M=(B_{BB}l_{2}{}^{2})^{1/3}/(B_{AA}l_{1}{}^{2})^{1/3}. \tag{1.7}$$

To determine the density with sufficient accuracy, the condition $x = 1$ can be replaced by the condition $y = 0$. We obtain

$$R_{c}\approx(1+\pi^{2}\varepsilon/16p_{0}{}^{2})^{1/\varepsilon}. \tag{1.8}$$

From this we obtain the values of ρ_A and ρ_B in the globule:

$$\rho_{A}\sim R_{c}^{-4/3}B_{AA}^{-1/3}\,l_{1}^{-2/3},\qquad \rho_{B}\sim R_{c}^{-4/3}B_{BB}^{-1/3}\,l_{2}^{-2/3}. \tag{1.9}$$

Let us now consider the case when $M\gg N$, and the molecule forms a globule with a coil-phase envelope consisting of B monomers. In this case the chemical potential of the B monomers should be continuous at the boundary of the globule nucleus,[8] i.e., in the language of the two-field model

$$\tau_{2}=\tau_{2}{}^{c},\qquad \chi_{2}{}^{-1}=0.$$

With the aid of the formulas (A.4)–(A.6) we obtain

$$(\eta_{A}-\eta_{B})/\eta_{B}\approx\varepsilon/2x,$$
$$F(\rho_{A})=-(64\pi^{2})^{-1}R_{c}{}^{-d}(1+x^{-1}-\varepsilon/4x-3\varepsilon/4x^{2}). \tag{1.10}$$

The density of the globule nucleus is given by the condition for a minimum of the free energy per monomer, $F(\rho_A)/\rho_A$, a condition which reduce at large R_c to the condition

$$x=1+\beta\varepsilon,\qquad \beta\sim 1. \tag{1.11}$$

The formulas (1.6)–(1.9) solve the problem of the density and composition of the globule nucleus. The density of the nucleus at low p_0 value depends on the composition of the molecule according to (1.11) (not a very marked dependence), and the composition of the nucleus also changes insignificantly—by an amount of the order of $\varepsilon/2$.

As a phase, the coil envelope can exist only in the case when the relation (1.10) for η_A and η_B is fulfilled in the nucleus. This means that an envelope forms around a large globule if M/N is greater than the value given by (1.7) by a factor of $(1 + \varepsilon/2)$. Naturally, in three-dimensional space the expansion in powers of ε has meaning only when it is regarded as an estimate for the universal coefficients, which do not depend on the details of the interaction between the monomers.

The line separating the regions of coil and globular states of the $A_N B_M$ molecule is given by the equation

$$\min\{(B_{AA} l_1^2 N^3)^{1/5}, \quad (B_{BB} l_2^2 M^3)^{1/5}\} \sim R_c \approx 1 + \pi^2/16 p_0^2.$$

In terms of the "new" monomers the globule nucleus is a concentrated solution, since the volume per (new) monomer is of the order of the intrinsic monomer volume R_c^3. Therefore, the virial expansion gave an incorrect answer. The new monomers are actually the blobs introduced by de Gennes.[11] The possibiity of the formation of globules from blobs is pointed out in Ref. 4.

The role of the θ point—the "coil–globule" transition point for an infinitely long molecule—is played by the temperature a which $B_{AB} = 0$. The coil–globule transition with respect to the parameter B_{AB} is, according to I. M. Lifshitz's classification,[8] a smooth second-order transition, but, in contrast to the cases investigated earlier, the coil is not Gaussian at the θ point: its size is determined by the scaling laws.

§2. A TWO-COMPONENT POLYMER SOLUTION

Let us consider a dilute solution of macromolecules A_N and B_M in a low-molecular solvent. We impose on the virial coefficients the same conditions as in §1:

$$B_{AA} > 0, \quad B_{BB} > 0, \quad B_{AB} < 0,$$
$$p_0^2 = B_{AB}^2 / B_{AA} B_{BB} \ll 1.$$

For the free energy per unit volume of such a solution we can write the virial expansion in the following form

$$\mathscr{F}(\rho_A, \rho_B) = N^{-1} \ln(\rho_A/\rho_A^*) + M^{-1} \ln(\rho_B/\rho_B^*) + B_{11} \rho_A^2 N^{-2} + B_{22} \rho_B^2 M^{-2} + 2 B_{12} \rho_A \rho_B M^{-1} N^{-1}. \tag{2.1}$$

Here B_{11}, B_{22}, and B_{12} are respectively the second virial coefficient for the A_N-A_N B_M-B_M, and A_N-B_M interaction, while ρ_A^* and ρ_B^* are respectively the density values at which the coils in the single-component solutions of the A_N and B_M molecules begin to touch each other:

$$\rho_A^* \sim N^{-4/5} (B_{AA} l_1^2)^{-3/5}, \quad \rho_B \sim M^{-4/5} (B_{BB} l_2)^{-3/5}.$$

The virial coefficients for large N and M have the form[9]

$$B_{11} = \lambda N^{9/5} (B_{AA} l_1^2)^{3/5}, \quad B_{22} = \lambda M^{9/5} (B_{BB} l_2^2)^{3/5},$$

where $\lambda \sim 1$ depends only on the dimensionality d of the space. We use the approximate value given by the Flory theory for the critical exponents.

The quantity B_{12} can be estimated as follows. So long as the dimension R of the molecules does not exceed R from (1.8), we can use the formulas (1.3) after setting $B_{12} = B_{AB}^R(R)$. In this case $B_{12}^2 < B_{11} B_{22}$, and the homogeneous solution is stable. Furthermore, for the homogeneous state to be stable, it is sufficient that the dimension of the molecules of only one species be not greater than R_c.

Let us now consider two molecule A_N and B_M with dimensions R_A and R_B such that $R_A, R_B > R_c$. Let us divide the A_N and B_M chains into $N/\mathscr{N}_A(R_c)$ and $M/\mathscr{N}_B(R_c)$ sections each of which has a dimension of the order of R_c. Using (1.3) and (A.9), we easily find that the second virial coefficient for the interaction between these sections is of the order of $-R_c^3/\sigma$, where $\sigma \sim 10^2$ is a large dimensionless parameter. Then, applying the Flory approximation to such effective monomers, i.e., regarding the A_N chains as one floating in a cloud of $M/\mathscr{N}_B(R_c)$ effective monomers of the B_M chain, we obtain the following estimate for B_{12}:

$$B_{12} \approx -MNR_c^3 / (2\mathscr{N}_A(R_c)\mathscr{N}_B(R_c)\sigma), \tag{2.2}$$

where R_c is given by the formula (1.8).

The solution will stratify if the equations

$$\begin{aligned} \mu_A(\rho_{A1}, \rho_{B1}) &= \mu_A(\rho_{A2}, \rho_{B2}), \\ \mu_B(\rho_{A1}, \rho_{B1}) &= \mu_B(\rho_{A2}, \rho_{B2}), \\ P(\rho_{A1}, \rho_{B1}) &= P(\rho_{A2}, \rho_{B2}) \end{aligned} \tag{2.3}$$

possess a solution in the case when $\rho_{A1} \neq \rho_{A2}$ and $\rho_{B1} \neq \rho_{B2}$. It follows from (2.1)–(2.3) that the two phases cannot be dilute solutions at the same time. Therefore, let us consider the case in which a condensate, i.e., a phase in which the correlation length is determined not by the length, but by the density, of the molecule entering into it, separates out in the solution. To compute the chemical potential of the monomers in the condensate, we must use the formulas from the Appendix. The equations (2.3) will in this case assume the form

$$\begin{aligned} &N^{-1} \ln(\rho_{A1}/\rho_A^*) + 2B_{12}\rho_{B1}/MN \\ &\quad = -[\varepsilon/2x - (\eta_{A2} - \eta_{B2})/\eta_{A2}] (4\mathscr{N}_A(R_c)\varkappa\varepsilon)^{-1}, \\ &M^{-1} \ln(\rho_{B1}/\rho_B^*) + 2B_{12}\rho_{A1}/MN \\ &\quad = -[\varepsilon/2x + (\eta_{A2} - \eta_{B2})/\eta_{A2}] (4\mathscr{N}_B(R_c)\varkappa\varepsilon)^{-1}, \\ &\rho_{A1}/N + \rho_{B1}/M + 2B_{12}\rho_{A1}\rho_{B1}/MN \\ &\quad = (\eta_{A2} + \eta_{B2}) [1 - x^{-1} + (\eta_{A2} - \eta_{B2})^2/\eta_{A2}^2\varepsilon] (16\varkappa)^{-1}. \end{aligned} \tag{2.4}$$

Here, as in §1, $\eta = \rho/\mathscr{N}(R_c)$. For rough estimates, we can neglect the quantity $x - 1$, and consider the condensate density to be a constant given by the equations (1.9). The condensate is a two-component semi-dilute polymer solution. Its composition is given by the first two equations from the system (2.4).

The equations (2.4), can, because of their complexity in the general case, be investigated only numerically. The completely symmetric case $M = N$, $\rho_A = \rho_B = \rho$, $B_{AA} = B_{BB} = B$, $l_1 = l_2 = l$ can be investigated analytically. Figure 1 shows the phase-state diagram in the N-ρ plane for this case. The quantities B, B_{AB}, and l are assumed to be fixed. The lower boundary of the region of two-phase states in the case when $N \gg \mathscr{N}(R_c)$ is given by the equation

$$\mathscr{N}(R_c) N^{-1} \ln(\rho/\rho^*) = -(8\varkappa)^{-1}, \tag{2.5}$$

and the upper bound in the condensate density, which we assume to be a constant, at least in the case when $N \gg \mathscr{N}(R_c)$. The critical point is given by the conditions

$$N/\mathscr{N}(R_c) \sim \sigma, \quad \rho \sim \rho^*(N) = N^{-4/5}(Bl^2)^{-3/5}.$$

Generally speaking, the equation (2.4) are inapplicable in the vicinity of the critical point for the stratification of the solu-

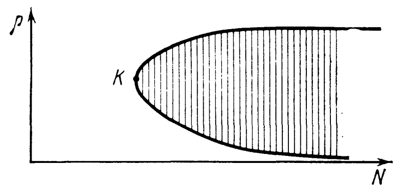

FIG. 1. Phase diagram of a two-component solution in the (N, ρ) plane in the symmetric case. The hatched region corresponds to the two-phase states; there exists a critical point K.

tion, since there occur here density fluctuations with scales much greater than R_c. In this case the density and the quantity R_c cannot be regarded as constants. The vicinity of the critical point requires special investigation, possibility, in the second ε approximation. Here the less dense phase can no longer be considered to be a dilute solution.

Figure 2 shows the phase-state diagram in the $|B_{AB}|$-ρ plane (also for the symmetric case). The quantities $B_{AA} = B_{BB}$ and N are fixed. The critical point and the boundaries of the two-phase region are given by the same equations as in the preceding case.

The $M \gg N, \rho_A/N \gg \rho_B/M$ case is, from the experimental standpoint, the most interesting case. In this region, we must distinguish between two experimentally observable effects: the coil–globule transition that occurs in each long molecule and the precipitation of a condensate. The formation of a globule corresponds to the appearance of a solution for the system of equations obtained from (2.3) when the second equation is replaced by the equation

$$\mu_B(\rho_{A2}, \rho_{B2}) = 2B_{12}\rho_{A1}/MN,$$

which expreses the equality of the free energy per monomer in the globular state to the corresponding quantity in the coil state. From this we obtain, after taking account of the condition $\rho_A \ll \rho_A^*$ for the solution to be dilute, as well as the fact that $\sigma \gg 1$, the equations

$$\mathcal{N}_A(R_c)N^{-1}\ln(\rho_A/\rho_A^*) = -(4\varkappa x)^{-1}, \tag{2.6}$$

$$\rho_A/\rho_A^*(\mathcal{N}_A(R_c)/N)^{9/5} = (1 - x^{-1} + \varepsilon/4x^2)(8\varkappa)^{-1}. \tag{2.7}$$

Equations (2.6) and (2.7) give in a parametric form the line $\rho_A = \rho_A(N)$ of first-order coil–globule phase transitions. But these equations were derived under the assumption that $|x-1| \sim \varepsilon$, and therefore correctly determine only that part of the transition line where

$$(\mathcal{N}_A(R_c)/N)^{9/5} \lesssim \sigma^{-1}. \tag{2.7}$$

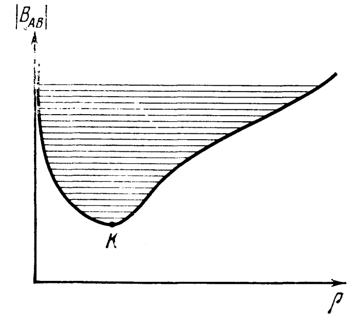

FIG. 2. Same as in Fig. 1, but in the $(\rho, |B_{AB}|)$ plane.

A special investigation is necessary for the computation of the critical degree of polymerization of the solution. In particular, we must extend the calculations carried out in the Appendix to the case $y \sim 1$.

We can determine in exactly the same way the conditions for the existence of a globule in the semidilute solution, which is specified by a single parameter: the density. To do this, we need only set in Eqs. (2.6)–(2.8)

$$\ln(\rho_A/\rho_A^*) \sim -1, \quad \rho_A/\rho_A^* \sim 1, \quad N \sim \rho_A^{-5/4}(B_{AA}l_1^2)^{-3/4}.$$

The inverse globule–coil transition also occurs, when ρ_A is increased, as a sharp first-order phase transition.

In all the preceding calculations we considered the globule and condensed-phase densities to be constants over the entire volume. In actual fact there is always a transition layer whose thickness in the region far from the critical point (see Figs. 1–3) is of the order of R_c. The free-energy density decreases continuously in the layer from its value in the less dense phase to its value in the denser phase. Hence we can estimate the globule-surface tension energy Σ per B_M molecule:

$$\Sigma \sim (M/\mathcal{N}_B(R_c))^{2/3}[\mathcal{N}_A(R_c)N^{-1}\ln(\rho_A/\rho_A^*) + (4\varkappa)^{-1}].$$

The equations (2.4) do not allow us to consider the precipitation of the globules, since they were derived under the assumption that the molecules outside the condensate are in the coil state. Therefore, we shall use another criterion: precipitation will occur if the surface-tension energy of a globule is equal to the entropy change that occurs when one molecule goes over from the precipitate into the solution. The condition for precipitation to occur has, in the usual units, the form $\Sigma \sim \ln(\rho_B^*/\rho_B)$. The solution temperature enters into this condition only through B_{AA}, B_{BB}, B_{AB}, and $l_{1,2}$.

In all the preceding calculations we assumed the condensate density to be a constant. This approximation is legitimate, since the density entered into the equations mainly through the parameter x, which is a slowly varying function

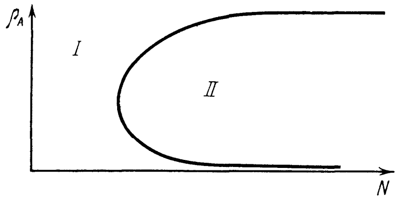

FIG. 3. Phase diagram in the (N, ρ_A) plane of a long poly-B chain in a solution of A_N molecules. The region I corresponds to the coil states; the region II, to the globular states. The curve separating them is a line of first-order phase transitions. The asymptotic forms of the branches of this line for large N have the form.

$$\mathcal{N}_A(R_c)N^{-1}\ln(\rho_A/\rho_A^*) = -(1+\varepsilon/4)/4\varkappa,$$

$$\rho_A = \text{const} \sim (\varkappa\mathcal{N}_A(R_c))^{-4/5}(B_{AA}l_1^2)^{-3/5}.$$

of the density. In almost all the cases the range of variation of x was of the order of ε. The condensate density, however, should vary quite strongly; in particular, it should depend markedly on the composition of the condensate. This dependence turns out to be quite universal. In the first place, it is clear that, with the exception of the just considered problem of the formation of globules in the solution, in all the situations considered above the condensate density will be maximal at $\eta_A = \eta_B$ (in the condensate). The condensate density will decrease as the composition deviates from this relation. Let us denote the condensate density for $\eta_A = \eta_B$ by $\rho_{\max}$; then

$$(\rho-\rho_{max})/\rho_{max}\sim(\Gamma(R_c))^{-1}(\eta_A-\eta_B)^2/\eta_A^2.$$

Since $\Gamma(R_c)\ll 1$, ρ possesses a fairly sharp peak. This prediction can be experimentally verified.

CONCLUSION

The results of the investigation pertain only to solutions of low concentration in the vicinity of the θ point of the interaction between monomers of different species, where B_{AB} is small. We did not also consider the vicinity of the critical point for the stratification of the semidilute two-component solution, since it is necessary here to take account of the blob-density fluctuations. This can be done by adding a magnetic field to the Hamiltonian (1.1) and using the second ε approximation.

Polymer complexes—the condensates produced in two-component polymer solutions—are a common practical realization of the objects described in the present paper. The available experimental data pertain largely to concentrated complexes, to which the results obtained above are not applicable. But the qualitative relationships remain valid: the degree of polymerization has a fairly large value that bounds from below the region of existence of a complex. It is also observed that the density of the complex depends quite critically on the composition. We must, however, make an important stipulation. A considerable amount of the experimental data pertains to polyelectrolytic complexes, which are formed as a result of the Coulomb interaction of the monomers in a solution of a strong electrolyte. If the concentration of the salt (electrolyte) is low, and the Debye length is much greater than the persistent length, then for the description of the interaction between the monomers we must use not the virial coefficients, but the Debye-Hückel theory. In this case the results obtained are not even qualitatively valid. But if the salt concentration is so high that its variation in the vicinity of a charged monomer is much smaller than the mean concentration value, then we can use the virial coefficients, and for such complexes the results obtained in the present paper are valid.

The best experimental verification of the results could be provided by experiments on complexes formed by the hydrogen bond, or by dipole or the van der Waals forces. We can vary the virial coefficients in such systems by regulating the salt or acid concentration.

I take the opportunity to express my profound gratitude to V. V. Shilov, who acquainted me with the experimental data, and to S. P. Obukhov, I. Ya. Erukhimovich, and A. Yu. Grosberg for numerous useful discussions.

APPENDIX

Here we describe the calculation of the free energy $F(\rho_A, \rho_B)$ by the methods of field theory. It is well known[6] that there occurs in the model with the Hamiltonian (1.1) in the case when $g_{12} < 0$ a first-order phase transition into the state with $\overline{\varphi}_1 \neq 0$, $\overline{\varphi}_2 \neq 0$. Let us find the thermodynamic potential $\Omega(\overline{\varphi})$ of the model in such a state. We shall use the well-known methods of computing the equation of state in the vicinity of a second-order phase transition point,[12,13] which are also expounded in Ref. 10.

The dominant contribution to $\Omega(\overline{\varphi})$ is made by ring skeleton diagrams (see Fig. 4). A line in the diagrams corresponds to a field-field correlation function in the absence of a condensate, which function has, for small wave vectors k, the form

$$\begin{aligned} G_1(\mathbf{k}) &= \langle\varphi_{1\alpha}(\mathbf{k})\varphi_{1\alpha}(-\mathbf{k})\rangle = [\chi_1^{-1} + (l_1^R)^2 k^2]^{-1}, \\ G_2(\mathbf{k}) &= \langle\varphi_{2\alpha}(\mathbf{k})\varphi_{2\alpha}(-\mathbf{k})\rangle = [\chi_2^{-1} + (l_2^R)^2 k^2]^{-1}. \end{aligned} \tag{A.1}$$

Here χ_1 and χ_2 are the susceptibilities for the fields φ_1 and φ_2 in the absence of interaction between the fields, i.e., in the case when $g_{12} = 0$:

$$\chi_{1,2} \sim (\tau_{1,2} - \tau_{1,2}^c)^{-\gamma}, \tag{A.2}$$

where γ is the critical exponent for the susceptibility, while τ_1^c and τ_2^c are respectively the critical points for the appearance of a condensate in the φ_1 and φ_2 fields. The quantities $l_{1,2}^R$ are, in the first ε approximation, determined by small distances, do not depend on $\tau_{1,2}$ and can be included in the normalization of the $\varphi_{1,2}$ fields.

The vertex functions in the diagrams for $\Omega(\overline{\varphi})$ are the sums of all the irreducible vertex diagrams, in which the lines correspond to the Green functions in the presence of a condensate. Therefore, the characteristic scale R, which must be substituted into the equations (1.3), is the density-density correlation length R_c for the monomers. Indeed allowance for the interaction with the condensate in the Green functions is equivalent to the consideration of the interaction of a given polymer with the remaining polymers in the solution. This interaction leads to a situation in which the scaling laws are "cut off" at distances of the order of R_c (Ref. 10).

The approximation used allows us to estimate only the most divergent part of $\Omega(\overline{\varphi})$, but this is not enough for us. Let

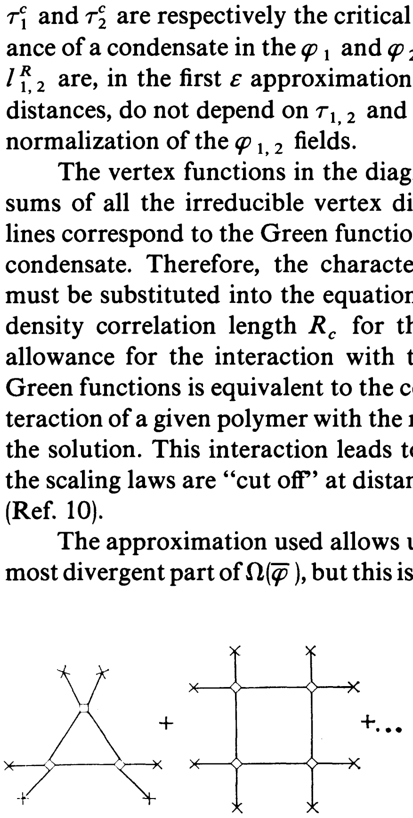

FIG. 4. The ring skeleton diagrams, which are summed in the Appendix. A line in the diagrams corresponds to the Green function for the field φ_1 or φ_2; a line with a cross, to the mean value $\overline{\varphi}_1$ or $\overline{\varphi}_2$; and a square, the sum of the irreducible vertex diagrams.

us introduce the dimensionless parameter $p_0 = |B_{AB}|/(B_{AA}B_{BB})^{1/2}$. We are considering the region $p_0 \ll 1$, $R_c \gg l$, where we can assume that

$$\Gamma_{11}(R_c)=\Gamma_{22}(R_c)=\Gamma(R_c)=\pi^2\varepsilon/4R_c^{\varepsilon}$$

and include l_1^R and l_2^R in the normalization of the φ_1 and φ_2 fields.

The sought sum of the ring diagrams constitutes a single-loop approximation for the renormalized Hamiltonian:

$$H^R(\varphi_R)=\int\Big\{\frac{1}{2}[\chi_1^{-1}\varphi_{R1}^2(\mathbf{x})+\chi_2^{-1}\varphi_{R2}^2(\mathbf{x})$$
$$+(\nabla\varphi_{R1}(\mathbf{x}))^2+(\nabla\varphi_{R2}(\mathbf{x}))^2]+\Gamma(R_c)(\varphi_{R1}^2(\mathbf{x})-\varphi_{R2}^2(\mathbf{x}))^2$$
$$+2y\varphi_{R1}^2(\mathbf{x})\varphi_{R2}^2(\mathbf{x})\Big\}d^dx,$$
$$y=\Gamma_{12}(R_c)/\Gamma(R_c)+1. \tag{A.3}$$

The fields φ_{R1} and φ_{R2} then have a physical meaning different from the physical meaning of the initially introduced φ_1 and φ_2. Let us make the following substitution in $H^R(\varphi_R)$:

$$\psi_{1,2\alpha}=(\varphi_{R1\alpha}\pm\varphi_{R2\alpha})/\sqrt{2}.$$

We obtain

$$H_R(\psi)=\int\Big\{\frac{1}{2}\Big[\Delta_1(\psi_1^2(\mathbf{x})+\psi_2^2(\mathbf{x}))+2\Delta_2\sum_\alpha\psi_{1\alpha}(\mathbf{x})\psi_{2\alpha}(\mathbf{x})$$
$$\times(\nabla\psi_1(\mathbf{x}))^2+(\nabla\psi_2(\mathbf{x}))^2\Big]+\frac{1}{2}y\Gamma(R_c)(\psi_1^2(\mathbf{x})+\psi_2^2(\mathbf{x}))^2$$
$$+2\Gamma(R_c)(2-y)\Big(\sum_\alpha\psi_{1\alpha}(\mathbf{x})\psi_{2\alpha}(\mathbf{x})\Big)^2\Big\}d^dx,$$
$$\Delta_1=\frac{1}{2}(\chi_1^{-1}+\chi_2^{-1}),\qquad \Delta_2=\frac{1}{2}(\chi_1^{-1}-\chi_2^{-1}).$$

When $\Delta_2\neq 0$ both fields separate out as a condensate, but one of them makes the dominant contribution: $\bar\psi_1\gg\bar\psi_2$. Since we are interested in the form of $\Omega(\bar\psi)$ in the region of small $\bar\psi_2$, we can make ψ_1 to be a constant, and integrate over the field ψ_2 after discarding the term $\Gamma(R_c)y(\psi_2^2)^2$. Assuming that

$$\Gamma(R_c)\psi_1^2\gg\Delta_1,\qquad |y|\ll 1,$$

we obtain the expression

$$\Omega(\psi_1)=(\Delta_1\psi_1^2+\Gamma y\psi_1^4)/2-\Delta_2^2/16\Gamma-2\Gamma^2\psi_1^4[(8\Gamma\psi_1^2)^{-\varepsilon/2}$$
$$-\Delta_1^{-\varepsilon/2}]/\pi^2\varepsilon,$$
$$\bar\psi_2=-\Delta_2/8\Gamma\psi_1,\qquad R_c^{-2}=8\Gamma\psi_1^2,\qquad \Gamma=\Gamma(R_c). \tag{A.4}$$

The second minimum of $\Omega(\psi_1)$ corresponds to a condensed (globular) state. The parameters Δ_1 and Δ_2 determine the density and thermodynamic functions of the condensaste. The condition $\partial\Omega/\partial\psi_1=0$ yields:

$$\Delta_1/2+y\Gamma\psi_1^2+2\Gamma^2\psi_1^2R_c^{\varepsilon}/\pi^2$$
$$+4\Gamma^2\psi_1^2(\Delta_1^{-\varepsilon/2}-R_c^{\varepsilon})/\pi^2\varepsilon+\varepsilon\Delta_2^2/32\Gamma\psi_1^2=0. \tag{A.5}$$

Setting

$$x=4\Gamma^2\psi_1^2R_c^{\varepsilon}/\pi^2\Delta_1\approx\varepsilon\Gamma\psi_1^2/\Delta_1,$$

we obtain from (A.5) the expression

$$\Omega(\psi_1,\psi_2)={}^1/_4\varepsilon\Gamma\psi_1^4(x^{-1}-1)-4\Gamma(\psi_1\psi_2)^2(1+{}^1/_4\varepsilon).$$

Representing x in the form

$$x=x_0+\delta x,\qquad \delta x\sim\Delta_2^2/(\Gamma\psi_1^2)^2,$$

we obtain for x_0 the equation

$$1+x_0+2x_0[(8x_0/\varepsilon)^{\varepsilon/2}-1+y]\varepsilon^{-1}=0.$$

Then in the first approximation in $\Delta_2^2/(\Gamma\psi_1^2)^2$

$$\delta x=-\Delta_2^2x_0[16(\Gamma\psi_1^2)^2((8x_0/\varepsilon)^{\varepsilon/2}-x_0^{-1})]^{-1},$$
$$\Omega(\psi_1,\psi_2)={}^1/_4\varepsilon\Gamma\psi_1^4(x_0^{-1}-1)$$
$$-4\Gamma(\psi_1\psi_2)^2\{1+{}^1/_4\varepsilon-\varepsilon[4x_0((8x_0/\varepsilon)^{\varepsilon/2}-x_0^{-1})]^{-1}\}. \tag{A.6}$$

It is not difficult to see that $\Omega(\psi_1,\psi_2)$ is the thermodynamic potential $\Omega=-PV$ of the corresponding polymer system. In the cases of interest to us $\psi_1\psi_2$ and x_0-1 are of the order of ε, and the formula (A.6) can be greatly simplified.

It remains to establish a correspondence between the renormalized quantity $\langle\varphi_R^2\rangle$ and the initial quantities ρ_A, ρ_B, and $\langle\varphi^2\rangle$. Using (A.4), we obtain

$$\langle\varphi_{R1}^2\rangle\approx{}^1/_2\langle\psi_1^2\rangle=\Gamma\psi_1^2/2\Gamma=R_c^{2-d}/4\pi^2\varepsilon.$$

Since

$$R_c^{-d}\sim\rho_A/\mathcal{N}_A(R_c),$$

we have

$$\langle\varphi_{R1}^2\rangle\approx 2R_c^2\rho_A(\varkappa\varepsilon\mathcal{N}_A(R_c))^{-1},\qquad \varkappa\sim 1.$$

As a result, we obtain the formula

$$P(\eta_A,\eta_B)=(\eta_A+\eta_B)[1-x^{-1}+(\eta_A-\eta_B)^2\eta_A^{-2}\varepsilon^{-1}](16\varkappa)^{-1}. \tag{A.7}$$

The free energy is

$$F(\eta_A,\eta_B)=\mu_A\rho_A+\mu_B\rho_B-P(\eta_A,\eta_B)$$
$$=(\eta_A+\eta_B)[-1-x^{-1}+(\eta_A-\eta_B)^2\eta_A^{-2}\varepsilon^{-1}](16\varkappa)^{-1}. \tag{A.8}$$

The quantities F and P assume their forms when they are expressed in terms of R_c. In that case

$$P=(64\pi^2)^{-1}(1-x^{-1})R_c^{-d}+{}^1/_2(\sqrt{\eta_A}-\sqrt{\eta_B})^2, \tag{A.9}$$
$$F=-(64\pi^2)^{-1}(1+x^{-1})R_c^{-d}+{}^1/_2(\sqrt{\eta_A}-\sqrt{\eta_B})^2.$$

We find, in complete agreement with the theory of phase transitions, that $F\propto R_c^{-d}$. As to the numerical factors, they have, of course, been estimated only in order of magnitude.

The applicability of the formulas (A.4)–(A.9) is limited by the conditions $\Delta_1\ll\Gamma\psi_1^2$ and $\Delta_2\lesssim\Delta_1$.

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[1] This explanation was offered by A. Yu. Grosberg and I. Ya. Erukhimovich during a discussion of the present paper. It is not suitable for quantitative computations, since it leads to incorrect results for the chemical potential of a monomer (see the Appendix), although it does give for the condensate density an estimate that is correct in the first approximation in ε (cf. (1.9)).

[2] We use the subscripts A and B to indicate the monomer species to which the quantity in question pertains. If these subscripts do not occur in some relation, then that relation is valid for either monomer species.

[3] We use, wherever it is legitimate to do so, the Flory values for the critical exponents.

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