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Phase diagrams classification of the systems with thermoreversible alternating association (the Flory approach)

M. V. Thamm and I. Ya. Erukhimovich^{a)} Physics Department, Moscow State University, Moscow, 119992 Russia

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We consider incompressible blends of f_1 - and f_2 -functional monomers A_{f_1} and B_{f_2} , capable of forming thermoreversible bonds AB only between unlike monomers with an equilibrium Arrhenius association constant $k = k_0 \exp(-\varepsilon/T)$. Effects of the parameters f_1 , f_2 , k_0 , and ε on the global phase behavior of these systems are analyzed within the conventional Flory approach. An explicit topological classification of all types of phase diagrams is given via building (i) the phase portraits, i.e., separation of the plane ($\ln k_0, \varepsilon$) into the regions corresponding to topologically similar phase diagrams, and (ii) typical phase diagrams on the (volume fraction; T) plane for all regions of the phase portraits. The phase behavior of the systems with alternating association is found to be rather sensitive to the values of the parameters $(\ln k_0, \varepsilon)$ and diverse. In particular, seven possible types of phase diagrams with topologically different binodals are found. Nontrivial phase behavior in the systems with alternating association includes closed immiscibility loops, triple points, metastable critical points, and even completely metastable phases. The main trend governing all the variety of these phase diagrams is an association-induced increase in the thermodynamic stability of blends of stoichiometric composition. In particular, low-temperature blends of stoichiometric composition turn out to be thermodynamically stable if $(-\varepsilon/2\Theta) > (f_1 + f_2)^{-1}$, where Θ is the value of the Θ temperature measured in energetic units. © 2003 American Institute of Physics. [DOI: 10.1063/1.1586253]

I. INTRODUCTION

The theoretical description of two- and multiplecomponent associating systems is of great theoretical and technological interest. From the practical point of view, this interest is also based on the fact that most of the solutions studied in biology (water solutions) and earth sciences (silicate melts) belong to the class of associating systems. The association of the components in these solutions is known to induce different types of interesting phase behavior (closed immiscibility loops, metastable critical points, eutectic points, and so on).¹ For example, water–water and water– PEO associations cause the closed immiscibility loops on the phase diagrams of PEO/water systems.^{2,3} Thus, it is important to learn which characteristics of association are responsible for one or another type of the phase behavior.

A theory describing the phase behavior of twocomponent associating systems should start obviously with some simple reference systems where the main tendencies governing this behavior can be easily investigated. The simplest example of such a referent system is that where all the associating particles are identical and bear identical functional groups *A* capable of forming thermoreversible saturated bond A-A with each other. This system, even if it includes also a nonassociation component, can be easily reduced to a one-component associating system and the corresponding theory is rather well developed.^{4–18} We refer to this system as that with self-association. The other basic model system (actually, the simplest irreducible two-component one) is a system where two sorts of identical associating particles are present, each particle bearing the identical functional groups only (say, A_{f_1} and B_{f_2}), and only unlike groups are capable of forming thermoreversible saturated bond A-B. We refer to this system as that with alternating association. It is both a good referent system and of certain physical interest itself, since some systems with donoracceptor interactions can be treated as those with alternating association. To our knowledge, the only theoretical studies of this class of associating systems were undertaken in Refs. 19-21. Tanaka and Ishida^{19,20} have stressed that the most characteristic peculiarity of the systems under consideration is the increase in thermodynamic stability of the blends with stoichiometric concentration. Patlazhan and Ladyzhinsky²¹ have found a possibility of phase diagrams with closed immiscibility loops in these systems. However, there are some inaccuracies in the aforementioned papers we address later in more detail. Thus, even a thorough investigation of the thermodynamics of systems with alternating association in the framework of the most commonly used Flory gelation theory^{22,23} is a still unsolved and interesting objective.

However, in the present paper we address the even more ambitious problem of topological classification of all phase diagrams possible in the systems under consideration. The procedure to solve this problem (which is, actually, just a simplified version of catastrophe theory²⁴) has been applied to analyze the phase behavior of one-component thermoreversible gels^{12,17} and the coil-globule transition in the presence of self-associating solvent.¹⁸ Here we apply this proce-

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^{a)}Electronic mail: ierukhs@polly.phys.msu.ru



FIG. 1. The typical clusters of bonds formed in the system with alternating association. A and B functional groups are shown by solid and dashed lines, respectively. (a) $f_1=f_2=3$ and (b) $f_1=3$, $f_2=2$.

dure to a new associating system: i.e., that with alternating association.

The further presentation is organized as follows: In Sec. II we describe the model and calculate the free energy of the systems with alternating association. Section III, which plays the central role in the paper, is devoted to the classification of phase diagrams itself. In Sec. III A we explain the general procedure of the phase diagrams construction and classification and derive the equations defining the critical points of the system. In Secs. III B and III C we present the classification of phase diagrams—i.e., plot the phase portraits and examples of all topological types of phase diagrams for the symmetric and asymmetric systems, respectively. Finally, Sec. IV includes a brief summary and some discussion of the results of the paper.

II. FREE ENERGY OF THE SYSTEM WITH ALTERNATING ASSOCIATION

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In this paper we consider the system consisting of two types of molecules A_{f_1} and B_{f_2} , bearing, respectively, f_1 and f_2 functional groups A and B capable of forming thermoreversible bond between each other (see Fig. 1):

$$\begin{array}{l} A+B \leftrightarrow AB, \\ k(T) \end{array}$$
(1)

where *T* is the temperature measured in energetic units (the Boltzmann constant is set to unity) and k(T) is an equilibrium constant of the reaction.

Following Lifshitz,²⁵ we assume the free energy of the system described above to be a sum of the structural and energetic contributions:

$$\mathbf{F}(\rho_1, \rho_2) / VT = F_{str}(\rho_1, \rho_2) + F^*(\rho_1, \rho_2), \qquad (2)$$

where *V* is the total volume of the system and ρ_1 , and ρ_2 are the concentrations (number densities) of the monomers A_{f_1} and B_{f_2} , respectively.

The contribution of usual (van der Waals) volume interactions into free energy we assume to be consistent with the Flory–Huggins theory:

$$F^* = -T\chi\phi_1\phi_2,\tag{3}$$

where the volume fractions $\phi_i = \rho_i v$ obey the incompressibility condition

$$\phi_1 + \phi_2 = 1 \tag{4}$$

and we presume for simplicity that the excluded volumes v of the components are equal.

Now, to calculate the structural contribution into Eq. (2) we use, in the present paper, the Flory approach of the theory of thermoreversible gelation.^{13,15,26} As shown in Ref. 13, within this approach the structural free energy can be written as follows:

$$F_{str}(\rho_{1},\rho_{2}) = F_{id}(\rho_{1}) + F_{id}(\rho_{2}) + \min_{\{\rho_{a}\}} F_{choice}^{f_{1}}(\rho_{1},\rho_{a}) + F_{choice}^{f_{2}}(\rho_{2},\rho_{a}) + F_{bond}(\rho_{a})].$$
(5)

Here the first two terms are just the free energies of ideal gases of $A_{f_1}(B_{f_2})$ monomers:

$$F_{id}(\rho) = \rho \ln \rho/e. \tag{6}$$

The third and fourth terms are just the free energies of the redistribution of all the $f_1\rho_1(f_2\rho_2)$ functional groups of the sort A(B) present per unit volume into ρ_a reacted and $f_i\rho_i - \rho_a$ unreacted ones:

$$F_{\text{choice}}^{f_i}(\rho_i,\rho_a) = f_i \rho_i [\Gamma_i \ln \Gamma_i + (1 - \Gamma_i) \ln(1 - \Gamma_i)], \quad (7)$$

where the conversions $\Gamma_i = \rho_a / f_i \rho_i$, i = 1,2, are introduced. The last term in Eq. (5) is the free energy of bond formation itself, which is as follows:²⁶

$$F_{\text{bond}}(\rho) = -\rho \ln g \rho/e.$$
(8)

Carrying out the minimization prescribed in Eq. (5) one finds the final expression for the structural contribution into free energy:

$$F_{str}(\rho_1, \rho_2) = \sum_{i=1,2} F_{id}(\rho_i) + f_i \rho_i [\ln(1 - \Gamma_i) + \Gamma_i/2],$$
(9)

where the conversions $\Gamma_{1,2}$ are related to the densities $\rho_{1,2}$ by the mass action law

$$f_1 k \rho_1 = \Gamma_2 / [(1 - \Gamma_1)(1 - \Gamma_2)],$$

$$f_2 k \rho_2 = \Gamma_1 / [(1 - \Gamma_1)(1 - \Gamma_2)].$$
(10)

It is worth noticing that the structural contributions to the free energy used by Tanaka and Ishida both in Ref. 19 based on the Stockmayer gelation model²⁷ and in Ref. 20 claiming to follow the Flory model differ from ours. This difference is due to important inaccuracies made in Refs. 19 and 20 under estimation of the free energy of the infinite cluster of the thermoreversible bonds (see discussion in Refs. 15 and 26 and, in more detail, in Ref. 28.) This inaccuracy leads to some unphysical singularities of the structural (and, therefore, total) free energy at the sol-gel threshold contradictory to the conventional Flory approach used, for example, in Refs. 3–7, 9–13, 15–18, and 26).

In the next section, we will give a full classification of phase diagrams, possible in the system with free energy described by Eqs. (2), (3) and (9), (10).

III. PHASE DIAGRAM CLASSIFICATION

A. General remarks

Before we start the phase diagram classification itself, it is worth expressing the total free energy of the system as a function of one of the monomers' volume fraction. Substituting Eqs. (3) and (10) into Eq. (2) and changing ϕ_1 into ϕ and ϕ_2 into $1-\phi$, one gets the following final expressions for the free energy of a system with alternating association and for the mass action laws, respectively:

$$F(N,T,\phi)/NT$$

$$=f(\phi) = \phi \ln(f_{1}!\phi/e) + (1-\phi)\ln[f_{2}!(1-\phi)/e]$$

$$+f_{1}\phi \ln(1-\Gamma_{1}) + f_{2}(1-\phi)\ln(1-\Gamma_{2})$$

$$+[f_{1}\phi\Gamma_{1}+f_{2}(1-\phi)\Gamma_{2}]/2 + \chi\phi(1-\phi), \qquad (11)$$

$$\kappa f_1 \phi = \frac{\Gamma_2}{(1 - \Gamma_1)(1 - \Gamma_2)},$$

$$\kappa f_2(1 - \phi) = \frac{\Gamma_1}{(1 - \Gamma_1)(1 - \Gamma_2)},$$
(12)

where the dimensionless association constant $\kappa = k/v$ is introduced.

The relationship between the volume fraction and conversions follows from Eqs. (4) and (10):

$$\frac{\phi}{1-\phi} = \frac{f_2 \Gamma_2}{f_1 \Gamma_1}.$$
 (13)

According to formulas (11) and (12) the free energy of the spatially homogeneous system with alternating association can be written as follows:

$$\mathbf{F}(T, V, \phi) = VF(T, \phi). \tag{14}$$

In case of a multiphase (say, n-phase) system the free energy is to be written as follows:

$$\mathbf{F}(T, V, \phi) = V \min_{\{\phi_i\}} \sum_{i=1}^n x_i F(T, \phi_i),$$
(14a)

where $x_i = V_i/V$ and V_i are the relative and absolute volumes of the *i*th phase and ϕ_i the volume fraction of A monomers in the *i*th phase. The equilibrium values of $\{x_i, \phi_i\}$ correspond to the minimum of the function (14a) with the values ϕ and T fixed and with due regard to the auxiliary conditions

$$\sum_{i=1}^{n} x_i = 1, \ \sum_{i=1}^{n} x_i \phi_i = \phi.$$
(15)

Thus, already at this stage of the investigation, one can find the equilibrium values of component densities in each of the phases for any given values of $\{\kappa, \chi, \phi\}$ and, therefore, plot a phase diagram of a system with some given dependences $\kappa(T)$ and $\chi(T)$. However, we address here a more ambitious goal—the problem of a full topological classification of the phase diagrams possible in the system. Therefore, to proceed further we should first analyze what peculiarities of phase diagrams are possible in the system under consideration.

It is well known²⁹ that there are four possible types of the special points on the phase diagrams of two-component incompressible systems: critical points, triple ones, those of equal concentration, and points of the phase transitions in pure components. One can easily see that, within the chosen approximation, in systems with alternating association there are no points of the latter two types. Indeed, these two peculiarities are characterized by the coexistence of two phases with equal composition. On the other hand, Eqs. (12) determine the conversions as some single-value functions of the volume fraction ϕ . Therefore, the free energy of the systems under consideration also is a single-value function of ϕ , which means that there is only one phase for every fixed value of ϕ . Thus, the phase diagrams of the systems with alternating association should be classified with respect to the critical and triple points only.³⁰

We start with consideration of the critical points. By definition, the critical points are determined by the following equations:²⁹

$$\partial^2 F / \partial \phi^2 = 0, \quad \partial^3 F / \partial \phi^3 = 0.$$
 (16)

The first of these equations defines the spinodal line $\phi_{sp}(T)$ on the phase diagram and the second one, which can be rewritten as $(\partial \phi_{sp}/\partial T)^{-1} = 0$, specifies the location of the critical point along the spinodal line. Substituting free energy (11) into the first equation of Eqs. (16) it is easy to get the spinodal condition as follows:

$$\frac{\partial^2 F}{\partial \phi^2} = \frac{1}{\phi(1-\phi)} - 2\chi + \kappa (1-\Gamma_1)(1-\Gamma_2) \\ \times \frac{2f_1 f_2 + f_1^2 \Gamma_1 + f_2^2 \Gamma_2}{1-\Gamma_1 \Gamma_2} = 0,$$
(17)

where the first two terms on the right-hand side correspond to the spinodal of the incompressible blend of two simple lattice liquids and the last one does to the association itself. One can rewrite Eq. (17) in terms of an effective χ parameter as follows:

$$\frac{\partial^{2} F}{\partial \phi^{2}} = \frac{1}{\phi(1-\phi)} - 2\chi_{\text{eff}} = 0,$$

$$\chi_{\text{eff}} = \chi - \kappa (1-\Gamma_{1})(1-\Gamma_{2})$$

$$\times \frac{2 f_{1} f_{2} + f_{1}^{2} \Gamma_{1} + f_{2}^{2} \Gamma_{2}}{2(1-\Gamma_{1}\Gamma_{2})}.$$
(17a)

An important feature of this effective parameter χ_{eff} is that, unlike the initial one χ , it substantially depends on the volume fraction since conversions Γ are related to the volume fraction by the mass action laws (12). Note that this fact was overlooked in Ref. 21 where the phase behavior of the system was assumed to be governed by a concentrationindependent (renormalized, though) Flory–Huggins parameter, which led the authors to some unphysical results like complete miscibility of the components at low temperatures.

The straightforward, even though somewhat cumbersome, calculation of the third derivative of the free energy results in the following expression:

$$\frac{\partial^{3} F}{\partial \phi^{3}} = -\frac{1-2\phi}{\phi^{2}(1-\phi)^{2}} + \frac{\Gamma_{1}\Gamma_{2}}{f_{1}f_{2}(1-\phi)(1-\Gamma_{1}\Gamma_{2})^{2}} \left\{ (f_{2}-f_{1})[f_{1}f_{2}(3+\Gamma_{1}\Gamma_{2})+f_{1}(f_{1}-f_{2})\Gamma_{1}+f_{2}(f_{2}-f_{1})\Gamma_{2}] + (f_{1}\Gamma_{1}-f_{2}\Gamma_{2})(2f_{1}f_{2}+f_{1}^{2}\Gamma_{1}+f_{2}^{2}\Gamma_{2})\frac{2-\Gamma_{1}-\Gamma_{2}}{1-\Gamma_{1}\Gamma_{2}} \right\} + \frac{\Gamma_{1}\Gamma_{2}}{\phi(1-\phi)}\frac{\kappa(1-\Gamma_{1})(1-\Gamma_{2})}{(1-\Gamma_{1}\Gamma_{2})^{3}} \left\{ 2f_{1}f_{2}(\Gamma_{1}-\Gamma_{2}) + f_{2}^{2}[(1-\Gamma_{2})-\Gamma_{2}^{2}(1-\Gamma_{1})]-f_{1}^{2}[(1-\Gamma_{1})-\Gamma_{1}^{2}(1-\Gamma_{2})] \right\},$$
(18)

where the first term determines location of the critical point of a lattice blend as is seen by setting $\Gamma_1 = \Gamma_2 = 0$. The parameters ϕ , κ , $\Gamma_{1,2}$ appearing in Eq. (18) are to obey the mass action laws (12). Thus, only two of these four variables are really independent. To retain the symmetry of the system, we excluded ϕ and κ , which enables us to rewrite the second equation of Eqs. (16) in terms of the conversions only:

$$(f_1^2 \Gamma_1^2 - f_2^2 \Gamma_2^2) (1 - \Gamma_1 \Gamma_2)^3 / (\Gamma_1 \Gamma_2)^2 = (f_1 \Gamma_1 + f_2 \Gamma_2) \{ 2 f_1 f_2 (\Gamma_1 - \Gamma_2) + f_2^2 [(1 - \Gamma_2) - \Gamma_2^2 (1 - \Gamma_1)] - f_1^2 [(1 - \Gamma_1) - \Gamma_1^2 (1 - \Gamma_2)] \} + (f_2 - f_1) (1 - \Gamma_1 \Gamma_2) [f_1 f_2 (3 + \Gamma_1 \Gamma_2) + f_1 (f_1 - f_2) \Gamma_1 + f_2 (f_2 - f_1) \Gamma_2] + (f_1 \Gamma_1 - f_2 \Gamma_2) (2 - \Gamma_1 - \Gamma_2) (2 f_1 f_2 + f_1^2 \Gamma_1 + f_2^2 \Gamma_2).$$

$$(19)$$

Unlike the critical points, the triple ones in the system under consideration can be found only numerically. They correspond to the situation where there is a tangent to the free energy (11) curve having three common points with it: i.e., the triple points are the solutions $\{\phi_1, \phi_2, \phi_3, T\}$ of the system

$$\frac{F(T,\phi_1) - F(T,\phi_2)}{\phi_1 - \phi_2}$$

$$= \frac{F(T,\phi_2) - F(T,\phi_3)}{\phi_2 - \phi_3} = \frac{\partial F(T,\phi)}{\partial \phi} \Big|_{\phi = \phi_1}$$

$$= \frac{\partial F(T,\phi)}{\partial \phi} \Big|_{\phi = \phi_2} = \frac{\partial F(T,\phi)}{\partial \phi} \Big|_{\phi = \phi_3}.$$
(20)

Having found the lines of triple and critical points, a further phase diagrams classification is to be done according to the strategy developed in Refs. 12, 17, and 18. This strategy can briefly be formulated as follows:

(i) The lines of critical and triple points are plotted on the $(\ln \kappa, \chi)$ plane.

(ii) The temperature dependences of the κ and χ parameters are assumed to be as simple as possible, which means the Arrhenius dependence $\kappa = \kappa_0 \exp(-\varepsilon/T)$ for the association constant and $\chi = \Theta/2T$ dependence for the Flory–Huggins parameter. Then the ln $\kappa(\chi)$ dependence is linear:

$$\ln \kappa(\chi) = \Delta S - E\chi, \tag{21}$$

where $\Delta S = \ln \kappa_0$ and $E = 2\varepsilon/\Theta$ are the bond formation entropy and reduced energy, respectively. Thus, any temperature change in a system with given nature of the association corresponds to a movement on the $(\ln \kappa, \chi)$ plane along a straight line whose slope and free coefficient are specific just for this kind of association. The straight line (21) is also plotted on the $(\ln \kappa, \chi)$ plane.

(iii) The numbers of intersections of the straight line (21) with the lines of critical (16) and triple (20) points are counted. If the line (21) intersects, say, the line of the critical

points, the values of $\ln \kappa$ and χ corresponding to any of such intersection satisfy both Eqs. (16) and (21), which means that there is a critical point on the phase diagram of the system under consideration and the values of $\ln \kappa$ and χ at this point are those defined by the intersection. Therewith the number of the intersections is just the number of all critical points on the phase diagram. On the contrary, if there are no intersections of these curves, then simultaneous equations (16) and (21) have no physical solution for the given system, and, therefore, the corresponding phase diagram has no critical points. The same considerations are valid for intersections of the line of the triple points (20) and straight line (21), which completely define location of the triple points.

(iv) The phase diagrams of two systems with different ΔS and *E* are said to belong to the same topological class if one can continuously transform the corresponding straight lines (21) one into another conserving the number of intersections between the straight line and the lines of critical and triple points throughout all the transformation. Obviously, the phase diagrams of these two systems also can be converted one into another by a continuous transformation, which conserves the number of critical and triple points.

(v) The plane of parameters ($\Delta S, E$) is separated into the regions in any of which some particular topological type of phase diagrams (i.e., some particular set of critical and triple points) is realized. Such a "map" is referred to as the phase portrait of the system.

(vi) A typical phase diagram is presented for each region of the phase portrait.

The resulting phase diagram classification obtained via the procedure described above depends on the fact whether the system under consideration is symmetric $(f_1=f_2)$ or not. So we consider these two cases separately, starting with more simple symmetric case.

B. Symmetric systems

1. Critical points

If $f_1=f_2=f$, some of the terms in Eq. (19) cancel each other so that it takes the form

$$(\Gamma_{1} - \Gamma_{2}) \{ (\Gamma_{1} + \Gamma_{2})(1 - \Gamma_{1}\Gamma_{2})^{3} - f(\Gamma_{1}\Gamma_{2})^{2} [(3 - \Gamma_{1}\Gamma_{2})(\Gamma_{1} + \Gamma_{2}) + 4] \} = 0.$$
(22)

One of the roots of this equation is

$$\Gamma_1 = \Gamma_2. \tag{23}$$

As could be easily checked using Eq. (13), in symmetric systems the equal conversions occur only for the symmetric blend with $\phi_1 = \phi_2 = 1/2$. Thus, in the symmetric systems there is a symmetric critical point with $\phi = 1/2$. Substituting Eq. (23) into Eqs. (17) and (12) we get the Flory-Huggins parameter and association constant in this critical point:

$$\chi = 2 + 2 f \Gamma / (1 - \Gamma), \quad \kappa = 2 \Gamma / f (1 - \Gamma)^2,$$
 (24)

where $\Gamma = \Gamma_1 = \Gamma_2$ is the conversion in the symmetric critical point.

Other roots of Eq. (22) are to satisfy the equation

$$(\Gamma_{1} + \Gamma_{2})(1 - \Gamma_{1}\Gamma_{2})^{3} = f(\Gamma_{1}\Gamma_{2})^{2}[(3 - \Gamma_{1}\Gamma_{2})(\Gamma_{1} + \Gamma_{2}) + 4].$$
(25)

This equation is symmetric with regard to the replacement $\Gamma_1 \leftrightarrow \Gamma_2$. Therefore, its roots (if any) are pairs of critical points, the conversions and volume fractions in which obey the relations

$$\Gamma_1^{(1)} = \Gamma_2^{(2)}, \ \Gamma_2^{(1)} = \Gamma_1^{(2)}, \ \phi^{(1)} = 1 - \phi^{(2)},$$
 (26)

where the upper coefficient enumerates the critical points in the pair. The roots of Eq. (25) are parametrized by substituting $b = \Gamma_1 + \Gamma_2$, $u = \Gamma_1 \Gamma_2$:

$$b = \frac{4fu^2}{(1-u)^3 - fu^2(3-u)}, \quad \Gamma_{1,2} = \frac{b \pm \sqrt{b^2 - 4u}}{2}.$$
 (27)

Substituting these solutions into the spinodal equation (17) and mass action law (12) one gets the expressions for the characteristics of the system in the critical points under consideration:

$$\chi = b^2 \frac{1 + (1 - f)u^2}{4u^2} = \frac{4f^2 u^2 (1 + (1 - f)u^2)}{[(1 - u)^3 - fu^2 (3 - u)]^2},$$



FIG. 2. The lines of critical points in the symmetric system for f = 1, 2, 3, 4. The solid lines correspond to the critical points with $\phi=0.5$: the dashed lines correspond to the pairs of asymmetric critical points.

$$\kappa = \frac{4u^2}{(1+u)[(1-u)^3 - fu^2(3-u)] - 4fu^2},$$

$$\phi(1-\phi) = \frac{[(1-u)^3 - fu^2(3-u)]^2}{16f^2u^3} = \frac{u}{b^2},$$

$$\phi = \sqrt{\frac{u}{b^2}\frac{\Gamma_2}{\Gamma_1}} = \frac{1 \pm \sqrt{1-4u/b^2}}{2}.$$
(28)

Equations (24) and (28) define parametrically the lines of critical points on the $(\ln \kappa, \chi)$ plane. These lines for the different values of f are shown in Fig. 2. The bold and dashed lines correspond to the symmetric critical points given by Eq. (24) and the pairs of asymmetric ones given by Eq. (28), respectively. In the limit of $\ln \kappa \rightarrow -\infty$ there is a single (symmetric) critical point with $\chi_{crit}=2$ as it should be in the case of no association at all. In the limit of $\ln \kappa \rightarrow \infty$ the dashed lines in Fig. 2 have vertical asymptotes whose physical meaning is rather clear. Indeed, in the case of large association constant almost all bonds have reacted and, therefore, the system under study could be considered as a mixture of the pure A component and AB associates (if $\phi < 1/2$) or that of the pure B component and AB associates (if $\phi > 1/2$). In any of these two regions we are expecting a usual phase diagram with one critical point defined by some renormalized value of χ . It follows from Eq. (28) that the value of this χ_{∞} is

$$\chi_{\infty} = (1+u_{\infty})^2 \frac{(1+(1-f)u_{\infty}^2)}{4u_{\infty}^2},$$
(29a)

where u_{∞} is the lower positive root of the equation

$$[(1-u_{\infty})^3 - fu_{\infty}^2(3-u_{\infty})](1+u_{\infty}) = 4fu_{\infty}^2.$$
(29b)

For instance, $\chi_{\text{crit}} = 3 + 2\sqrt{2}$ in the case of f = 1.

Finally, it follows from Eq. (24) that the branch of critical points line corresponding to large χ has a logarithmlike form in the limit $\chi \rightarrow \infty$: $\ln \kappa \sim \ln \chi$. Let us mention also a branching point on the line of critical points, where the pair of critical points first occurs, branching off the critical points with $\phi = 1/2$. It is easy to see that for the values of parameters corresponding to this branching point and for $\phi = 1/2$ the first nonzero derivative of the free energy is $\partial^7 F/\partial \phi^7$ (all even derivatives of the free energy equal zero due to the symmetry of the system).

It is important to emphasize that in the Flory approximation we use here the arrangement of critical points lines depends only quantitatively on the functionality of the monomers. Therefore, some particular topological types of the phase diagrams do or do not exist independently on the value of f. For example, the topological types of phase diagrams of the systems with f=1, where only dimers can appear, are the same as in the system with $f \ge 3$, where an infinite cluster of bonds may arise. The only difference between the systems with different functionalities is in the particular values of the reduced energy and entropy of the bond necessary for occurrence of this or that type of phase diagrams. Due to this peculiarity of the system under consideration, the phase por-



FIG. 3. The lines of critical and triple points for the symmetric system with f=3. The thick line is the line of triple points, thin lines the lines of critical points. The straight line shows an example of a section, which includes the triple point [the corresponding phase diagram is shown in Fig. 5(d)].

traits of all symmetric systems with alternating association are topologically identical. For definiteness, in what follows we choose f=3.

2. Triple points

Let us now discuss whether triple points may be observed in the system. One can easily see that some of the phase diagrams (for example, the one corresponding to the straight line in Fig. 3) have a pair of high-temperature critical points. It is natural to expect that at least some of these phase diagrams should include also a triple point between the critical points mentioned above. The volume fraction corresponding to this triple point should obviously be $\phi = 1/2$ due to the symmetry of the system. To find the line of triple points (the bold line in Fig. 3) we numerically solved Eq. (20). In the low-temperature (high- χ) limit this line has an asymptote with the slope $(2 f)^{-1} = 1/6$. This asymptote has a rather simple physical meaning: the highly intraconnected phase with $\phi = 1/2$ is thermodynamically stable if the association energy per one molecule is larger than the Flory-Huggins one:

$$\varepsilon f/2 > \Theta/2 \rightarrow E = \varepsilon/2\Theta > (2 f)^{-1}. \tag{30}$$

3. Phase portrait

The next step in the phase diagrams classification is to construct the phase portrait of the system on the $(\Delta S, E)$ plane (the latter parameters being the dimensionless entropy and energy of the bond: i.e., free term and slope of an arbitrary straight line on the $(\ln \kappa, \chi)$ plane). The aforementioned phase portrait given by Fig. 4 includes (i) the lines corresponding to the set of tangent lines to the lines of critical and triple points (curves 1 and 2 on Fig. 4), (ii) the line corresponding to the sheaf of lines passing through the branching point in Fig. 2 (line 3 in Fig. 4), and (iii) vertical lines E= 0 and E = -1/6 (lines 4 and 5 in the figure) separating the regions with different number of low-temperature (high- χ) intersections between the straight lines (21) and the lines of critical and triple points, respectively. [The number of intersections between the line of critical points and the straight



FIG. 4. The phase portrait of the symmetric system with f=3. The numbers are marking the lines of the phase portrait (for their meaning see the main text): the letters are marking the regions. For any region marked by "x" the example of corresponding phase diagram is given in Fig. 5(x).

lines (21) with some particular free coefficient ΔS and the slopes $E = \pm \varepsilon$ always differ by 1 if $\varepsilon > 0$ is small enough.]

Every region on the phase portrait constructed in such a way corresponds to a certain particular topological type of the phase diagrams. To describe the latter more precisely we need some additional classification of critical points. By definition, any critical point C is such a point (ϕ_C, T_C) that for $T > T_C$ (or $T < T_C$) the system becomes unstable with the respect to separating into two phases with almost equal compositions $(|\phi_1 - \phi_2| \rightarrow 0 \text{ when } T \rightarrow T_C)$. But some of such critical points (ϕ_C, T_C) may (due to presence of some other critical point) already belong to the region unstable with respect to separating into phases with finite difference of compositions. We will refer to such critical points as the metastable ones. The curves on the phase portrait which separate the regions with different sets of such metastable critical points (say, with different topology of spinodal lines) but with the same set of the thermodynamically stable peculiarities of phase diagrams (or, say, with the same topology of binodal lines) are given by dashed lines in Fig. 4.

4. Phase diagrams

Let us now consider all the types of phase diagrams corresponding to the different regions on the phase portrait. Even though both *E* and ΔS are constant parameters for any real system, we use the expressions like "increase of *E*" rather widely with the purpose to describe evolution of the global phase behavior when varying the systems with different *E* and ΔS .

5. Low association at any temperature

This takes place if ΔS is sufficiently less than zero and *E* is positive. The phase diagrams of this type are shown on Fig. 5(a), which is similar to the trivial phase diagram of a nonassociating two-component blend.

6. High association at low temperature

As *E* passes zero the association begins to increase with the decrease of temperature. If *E* stays higher than -1/6, a





metastable critical point arises on the phase diagram [see Fig. 5(b)]. In this case the association constant tends to infinity at low temperatures but the condition (30) is still not valid. Thus, a homogeneous phase with nearly stoichiometric composition (i.e., close to $\phi = 1/2$) may exist below such a critical point. It is important to stress that this phase is still metastable for any temperature lower than $T_{\rm crit}$. In the systems with E < -1/6 the low-temperature phase with stoichiometric composition (PSC) becomes thermodynamically stable at sufficiently low temperature triple) point²⁹ appears on the phase diagram [see Fig. 5(c)].

7. High association at high temperature

This occurs if the high-temperature limit of the association constant, ΔS , is large enough. If E>0 (i.e., association decreases with the increase of temperature), the corresponding phase diagram contains a triple point [see Fig. 5(d)]. The rise of this triple point is due to the fact that at high temperature, when association is strong, the blend with nearly stoichiometric composition (BSC) is thermodynamically more favorable then any other blends. Now, if the energy of the bond *E* becomes negative, in addition to the aforementioned high-temperature triple point a metastable PSC similar to that on Fig. 5(b) appears on the phase diagram [see Fig. 5(e)]. If *E* decreases further (but still E > -1/6), the two metastable critical points on the phase diagram may merge and so the BSC turns to be at least metastable at all temperature ranges [see Fig. 5(f)].

8. High association at any temperature

The further evolution of phase diagrams with the diminishing of *E* depends very much on the value of ΔS . If ΔS is sufficiently large (i.e., when association is very strong at all temperatures), the BSC becomes thermodynamically stable as soon as the bond energy turns lower then the critical value of -1/6. The corresponding phase diagram is shown on Fig. 5(g). As consistent with the discussion above, in the case of high association the phase diagram is a combination of the phase diagrams of two nonassociating systems A + AB and

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AB+B. Now, if the entropy of the bond ΔS is not large enough, the crossing of critical value E = -1/6 leads to appearance of low-temperature stable FSC, which can be accompanied by both a pair of metastable critical points and a continuous corridor of metastability [Figs. 5(h) and 5(i), respectively]. Note that while energy *E* is decreasing (with ΔS staying constant), the phase diagram of Fig. 5(h) first proceeds into one shown at Fig. 5(i) and, with further diminishing, into the phase diagram shown at Fig. 5(g).

Two more topological types of phase diagrams including the closed immiscibility loops may occur if both the entropy and energy of the bond are negative and large in absolute value (which means that the association is low at high temperatures and increases drastically while temperature decreases). These phase diagrams are shown on Figs. 5(j) and 5(k). The physical reason for these diagrams to appear is as follows. At high temperatures the association is almost absent and phase diagrams of Figs. 5(j) and 5(k) are almost similar to that on Fig. 5(a). When temperature decreases association becomes more and more strong and therefore the mixture stabilizes. Depending on the values of parameters, such stabilization may result to appearance of the symmetric lower critical solution temperature (LCST) [Fig. 5(i)] or a pair of asymmetric LCST separated by the triple point of stoichiometric concentration [Fig. 5(k)]. At last, at the low temperatures the association is very strong and therefore phase diagrams of Figs. 5(j) and 5(k) are similar to one given by Fig. 5(g).

Summarizing the results of this section, we found seven different topological types of phase diagrams possible in symmetric systems with alternating association at different entropy and energy of the bond. The number of topologically different types of phase diagrams increases to 11 if the metastable critical points are included. The main trend governing all the variety of these phase diagrams is an associationinduced increase in the thermodynamic stability of BSC

In the next section we analyze the phase behavior of the asymmetric systems with alternating association. Naturally, we expect in this case even higher diversity of phase diagrams as, on the one hand, the main physical trend being the rise of thermodynamic stability of the BSC is retained and, on the other hand, the special symmetry of the phase diagrams with respect to the transformation $\phi \leftrightarrow 1 - \phi$ is removed.

C. Asymmetric systems

1. Critical points

Let us apply the procedure of the phase diagrams classification to the general case of asymmetric systems with $f_1 \neq f_2$. Using the mass action laws (12) and the spinodal equation (17) it is easy to express the spinodal values of the association constant, Flory–Huggins parameter and volume fraction as functions of conversions:

$$\kappa = \frac{f_1 \Gamma_1 + f_2 \Gamma_2}{f_1 f_2 (1 - \Gamma_1) (1 - \Gamma_2)},$$
(31a)



FIG. 6. The lines of critical points of the asymmetric systems for $f_1 = 3$ and $f_2 = 1$ (dashed line), 2 (thick line), 3 (thin line), and 4 (dotted line).

$$2\chi = \frac{(f_1\Gamma_1 + f_2\Gamma_2)^2}{f_1f_2\Gamma_1\Gamma_2} + \frac{f_1\Gamma_1 + f_2\Gamma_2}{1 - \Gamma_1\Gamma_2} \times (2 + \Gamma_1f_1/f_2 + \Gamma_2f_2/f_1),$$
(31b)

$$\phi = \frac{f_2 \Gamma_2}{f_1 \Gamma_1 + f_2 \Gamma_2}.$$
(31c)

Substitution of the spinodal conversions $\Gamma_1(\kappa,\chi), \Gamma_2(\kappa,\chi)$ defined by Eqs. (31) into Eq. (19) gives the lines of critical points on the $(\ln \kappa, \chi)$ plane. These lines are plotted on the Fig. 6 for the case of $f_1=3$, f_2 =1,2,3,4. One can see that in the case of $f_1 \neq f_2$ these curves have two disconnected branches. The first, monotonous high-temperature (low- χ) one approaches the trivial critical point $\chi=2, \phi=0$ in the limit of $\kappa \rightarrow 0$. When κ increases, the critical value of χ also increases and the critical composition ϕ_c shifts toward the pure low-functional component (i.e., increases for $f_2 = 1, 2$ and decreases for $f_2 = 4$). In the limit of high association $\kappa \rightarrow \infty$ almost all bonds have reacted and the high-temperature branch of critical points line approaches the critical point of the mixture of the pure L component and stable LH associates, L and H being the lowand high-functional components, respectively. The second, low-temperature branch, in turn, consists of two curves separated by the cusp. The low- χ curve approaches in the limit of $\kappa \rightarrow \infty$ the critical point of the mixture of the stable LH associates and pure H component. Note that in the symmetric case the aforementioned LH/H and LH/L systems are physically identical and therefore two lines of critical points with vertical asymptotes degenerate in this case into one "double" line as discussed in the previous section. The high- χ branch of the critical points line once again has a logarithmlike form in the limit $\chi \rightarrow \infty :\ln \kappa \sim \ln \chi$. In this limit the critical composition ϕ_c is equal to the stoichiometric one $\phi_{st} = f_2/(f_1 + f_2)$ and it shifts towards the pure H component (i.e., decreases for $f_2 = 1, 2$ and increases for $f_2 = 4$) if χ is finite. Thus, the region of volume fractions between $\phi = 0.5$ and ϕ_{st} never includes any critical points.

2. Triple points

In Fig. 7 the lines of critical (thin) and triple (thick) lines for this system are shown. Similarly to the case of symmetric



FIG. 7. The lines of critical (thin line) and triple (thick line) points of the asymmetric system with $f_1=2, f_2=3$.

systems the line of triple points has an asymptote which slope in this case equals $(f_1+f_2)^{-1}$, which is the evident generalization of Eq. (30). Let us stress also an important difference from the symmetric case: now the line of triple points starts in a point *T* rather than in the cusp *C* of the critical points curve. The case is that in the symmetric case only pairs of critical points with *equal* critical temperature may exist and therefore there *should* be a triple point between them. But in the asymmetric case the equality of critical temperatures is not required and therefore the phase diagrams may include not only "critical-point–triple-point– critical-point," but also "critical-point–metastable-criticalpoint" combination.

Evidently, the distance between two branches of the critical line in the limit $\kappa \rightarrow \infty$ as well as that between the points *C* and *T* increases with increase of the difference $|f_2 - f_1|$ but the disposition of the critical and triple points lines stays the same. Thus, similarly to discussion of the symmetric systems above, one can expect that the topology of the resulting phase portraits of the asymmetric systems will not depend on the specific values of f_1, f_2 . Due to this reason, we have chosen in what follows $f_1=2$ and $f_2=3$ as the lowest values of functionalities for which infinite cluster may arise in the system.

3. Phase portrait

In Fig. 8 the corresponding phase portrait is shown. It includes the following six curves: (i) the curves corresponding to the set of tangents to the lines of the critical and triple points (curves 1 and 2 in the figure), (ii) those corresponding to the sheaf of the straight lines drawn through the cusp of the critical points line and the intersection between the critical and triple point lines (lines 3 and 4, respectively), and (iii) the vertical lines E=0 and $E=-0.2=-(f_1+f_2)^{-1}$ (lines 5 and 6) which separate the regions with different numbers of low-temperature critical and triple points.

Similarly to the symmetric case, we separate the regions with different binodal topology by the solid curves, and those, which differ only in the metastable peculiarities of phase diagrams, by the dashed ones.



FIG. 8. Phase portrait of the asymmetric $(f_1=2,f_2=3)$ system with alternating association. The area close to the line 4 includes plenty of minor details. To show them better we plotted the lines $\Delta(E) = (\ln \kappa_0)_i(E) - (\ln \kappa_0)_4(E)$, where $(\ln \kappa_0)_i(E)$ is an *i*th line of phase portrait, in the inset. The numbers are marking the lines of the phase portrait (for their meaning see the main text): the letters are marking the regions. For any region marked by "x" the example of corresponding phase diagram is given in Fig. 9(x).

4. Phase diagrams

In the case of *low association at any temperature*—i.e., for positive *E* and negative ΔS with sufficiently large $|\Delta S|$ —we get a trivial phase diagram with one critical point [Fig. 9(a)]. If the *association slowly increases with the decrease of temperature* (i.e., if -0.2 < E < 0), similarly to the symmetric case, a metastable phase with nearly stoichiometric concentration arises [see Fig. 9(b)]. On the contrary, the high- ΔS behavior of phase diagrams differs from that of the case of symmetric systems. The difference is that before the eutectic point arises on the phase diagrams there is also a region *c* where the phase diagrams have two metastable critical points [Fig. 9(c)]. The aforementioned peculiarities—the low- and high-temperature metastable critical points—may arise simultaneously [Fig. 9(d)] or even merge giving rise to a corridor of metastability of the BSC [see Fig. 9(e)].

Let us now consider the regions of the phase portrait corresponding to E > -0.2 and ΔS large enough. In this case the *association at high temperature is high* and it either decreases (if E > 0) or slowly increases (if -0.2 < E < 0) with the decrease of temperature. If *E* is positive, we have a phase diagram with eutectic point [Fig. 9(f)]. When the bond energy becomes negative, a metastable PSC arises [Fig. 9(g)], which accrete with a high-temperature metastable region with a further decrease of *E* [see Fig. 9(h)].

Phase diagrams with E < -0.2 correspond to *high association at low temperatures*. The main peculiarity of all this diagrams, similarly to the symmetric case, is the thermodynamic stability of a BSC in the low-temperature region. If the bond entropy, and, therefore, association at high temperature, is sufficiently small, the phase diagram differs from that given by Fig. 9(a) only by the presence of low-temperature PSC [see Fig. 9(i)]. In the regions (j), (k), (l), which are close



FIG. 9. The examples of phase diagrams of the asymmetric systems with $f_1 = 2, f_2 = 3$. The temperature is measured in the units of χ^{-1} (i.e., is renormalized by the factor $2/\Theta$: thick lines correspond to the binodals and thin lines to the spinodals. (a) E=0.1, ln $\kappa_0 = 0$; (b) E = 0.15, ln $\kappa_0 = 3$; (c) E= -0.175, ln $\kappa_0 = -1$; (d) E = -0.12, ln $\kappa_0 = 0$; (e) E = -0.16, ln $\kappa_0 = -0.2$; (f) E = 0.3, $\ln \kappa_0 = 6$; (g) E = -0.075, $\ln \kappa_0 = 1.1$; (h) E = -0.1, $\ln \kappa_0 = 2$; (i) E = -0.4, $\ln \kappa_0 = -3$; (j) E = -0.43, $\ln \kappa_0 = -2.92;$ (k) $E = -0.24, \ln \kappa_0$ =-1.24; (l) E=-0.33, ln $\kappa_0=-2$; (m) E = -0.4, $\ln \kappa_0 = -2$; (n) E=-0.6, $\ln \kappa_0 = -4.6$; (o) E = -1, $\ln \kappa_0 = -5;$ (p) $E = -0.24, \ln \kappa_0$ =-0.8; (q) E=-0.85, $\ln \kappa_0 = -7.4$. The inset shows an enlarged picture of the area within the dashed rectangle.

to the intersection of the lines 4 and 6 on the phase portrait (see Fig. 8), there are three more types of the phase diagrams. These phase diagrams differ from each other and from that shown on Fig. 9(i) by the number of metastable critical points and/or the presence of a metastable corridor of miscibility (MCM). Their appearance is due to merging of low- and high-temperature spinodals [Fig. 9(j), one metastable critical point and MCM], the appearance of a pair of new high-temperature metastable critical points [Fig. 9(k), three metastable critical points], and the combination of these two peculiarities [Fig. 9(l), three metastable critical points and MCM].

If ΔS is large enough and E < -0.2 (i.e., association is high at all temperatures), the phase diagram takes the form

shown on Fig. 9(m). As expected, it is just a combination of two trivial [similar to Fig. 9(a)] phase diagrams of two-component systems A + AB and AB + B. When ΔS decreases, one of the immiscibility regions on Fig. 9(m)(which with the predominance of the low-functional component) increases in size and acquires a specific hoodlike form (somewhat similar phase diagrams for one-component systems are found in Refs. 11 and 16). This deformation of the immiscibility region can entail two new peculiarities of phase diagrams. First, a pair of metastable critical points may arise at the hoodlike spinodal [Fig. 9(n)], and second, the upper part of the hood may break away from the lower part, giving rise to a phase diagram with a *closed* immiscibility loop [Fig. 9(0)]. This phase diagram corresponds to the situation when the straight line (21) intersects three times the tangentlike low- χ critical points curve in Fig. 7.

The last two types of phase diagrams shown in Figs. 9(p) and 9(q) correspond to E < -0.2 and intermediate values of ΔS . The reason for their appearence is that there are three different ways to transform a phase diagram with peritectic point [Figs. 9(i)-9(l)] into that with two immiscibility regions [Figs. 9(m) and 9(n)] via increasing ΔS :

(i) If |E| is sufficiently low (but not lower then 0.2), one starts with the phase diagram of Fig. 9(1), in which an eutectic point appears with the increase of ΔS [see Fig. 9(p)]. With an increase of ΔS the eutectic and peritectic points approach each other until, eventually, they merge, giving rise to the phase diagram type shown at Fig. 9(m).

(ii) If |E| is a bit larger, the peritectic type phase diagram [either of Fig. 9(j) or Fig. 9(l) type] just transforms into that with two immiscibility regions by adhesion of a triple point to the outer binodal line. As a result, the phase diagrams shown in Figs. 9(m) and 9(n) we discussed above appear.

(iii) If |E| is large enough, the inner and outer binodals merge at a temperature lower than that of the triple point, giving rise to the phase diagram shown in Fig. 9(q). The further increase of the bond entropy leads to transformation of this phase diagram into that shown in Fig. 9(n).

Thus, we listed the topological types of phase diagrams corresponding to all regions on the phase portrait.

IV. CONCLUSIONS

Thus, the global phase behavior of two-component systems with alternating association is governed by an association-induced increase in the thermodynamic stability of blends of stoichiometric composition and differs substantially from that of the systems with self-association, which is rather dependent on the fact if an infinite cluster of labile bonds occurs in the system.¹⁷ As consistent with the full topological classification of the phase diagrams we presented above within the framework of the conventional Flory approach, the phase behavior of the systems with alternating association is rather diverse. We found seven possible topological types of their phase diagrams, even distinguishing them only with respect to the topologically different binodals. If the metastable critical points are also taken into account, then the number of possible topological types increases up to 11 in the case of symmetric and up to 17 in the case of asymmetric systems. Nontrivial phase behavior in systems with alternating association is not exhausted by closed immiscibility loops, but includes also triple points (eutectics and pertectics), metastable critical points, and even completely metastable phases.

All these elements are far from being typical for liquid– liquid phase diagrams but often observed in the liquid–solid and solid–solid phase diagrams³² (in particular, for sulfide, oxide, and silicate systems, where the cation–anion interactions can be roughly modeled as forming of ionic bonds between the otherwise thermodynamically incompatible ions). We consider this fact as a qualitative confirmation of our theory because the difference between the solid and liquid states is beyond the accuracy of the Flory approximation to which we restricted ourselves in this work.

Indeed, this approximation does not allow for influence of some additional correlations due to cyclization (i.e., intracluster bonding), intracluster and intercluster van der Waals interactions, and the angle-dependent interactions between the bonds adjacent to the same monomer. Some of these additional correlations may lead to the occurrence of a crystal ordering in the systems under consideration. Despite many attempts to overcome this shortcoming, $^{4,6,7,13,15,17,26,33-37}$ the role of these correlations is still far from being clear. Thus, there are two reasons in favor of using here the Flory approximation elaborated earlier by one of us^{5,13} as well as other authors.^{6,9,10,15} First, this approximation is comparatively simple, and it is this feature which enabled us to carry out the full topological classification of the phase diagrams of the systems with alternating association. Second, the Flory approach is the most commonly used one in the scientific community, which enables the reader to concentrate on the main result of our consideration rather than query validity of a new approximation.

And this most important result of our consideration is that the phase behavior of the associating systems is not only governed by the qualitative characteristics of association (i.e., is it self- or alternating association, etc.) but also depends drastically on the quantitative characteristics of the bonds. More precisely, to predict the phase behavior of an associating system one should not only define its general characteristics (say, the type of association and monomers functionalities), but also measure the particular values of the entropy and energy of the bond and specify to which region of the phase portrait do these values correspond. In this respect, other approximations are expected to give only some new subtle details^{30,31} as compared to what is found within the Flory approximation. Evidently, the essential role of the quantitative characteristics of the bonds will remain in the more complex systems whose phase behavior we suppose to discuss elsewhere. We believe that further analysis along this vein could result in elaboration of strict quantitative theory of hydrophobic and hydrophilic interactions.

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