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Nature of double critical points in binary solutions

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The nature of the reentrant demixing transition in binary solutions with H bonds is studied in the framework of an Ising-like Hamiltonian with effective spin-spin interaction constant. It is taken into account that the internal variables describing the H-bond network are characterized by the spatial time scales essentially shorter than those for the spin variables. Due to this the contribution of H bonds to the effective spin-spin interaction constant is described by thermodynamic methods. With the help of the catastrophe theory the classification of possible types of phase diagrams leading to the double critical point is given. The influence of small quantities of third component (electrolytes, water, and molecules similar to CCl_4) is discussed.

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INTRODUCTION

The nature of the double critical point (DCP) and the properties of a system near it were the subject of numerous investigations (see Refs. [1–3]). Main attention was paid to binary and quasiternary solutions in which the appearance of a the DCP is connected with the formation of a strong H-bond network. As an example we can give the ‘‘guayacol-glycerin’’ solution [4]. Among many attempts to elucidate the role of H bonds we note (1) quasichemical approach [5]; (2) the modeling of the interparticle interactions with the help of decorated lattice models isomorphic to the standard Ising model [6–8]; and (3) the description of H bonds in the framework of the Hamiltonian formalism [9].

In Ref. [5] the original qualitative arguments of Hirschfelder *et al.* [10] about the role of H bond were subjected to quantitative analysis within the quasichemical approximation. It was shown that the competition of the effective intermolecular repulsion with the attraction initiated by the formation of H bonds can lead to the demixing diagram with upper and lower critical points. In Ref. [9] the formation of H bonds is modeled with the help of Potts variables. The application of the renormalization procedure in Refs. [11–13] allowed to achieve the adequate description of fluctuation phenomena near the upper and lower critical points as well as near the DCP. Besides, it was shown that, in principle, the proposed Hamiltonian is able to reproduce many characteristic features of phase diagrams of binary solutions [14], including the DCP. In Ref. [15] a rather more simple version of the Walker-Vause Hamiltonian [9] had been analyzed within the mean-field approximation and all conclusions made in Ref. [14] about the structure of phase diagrams were confirmed. It was shown that the internal Potts variables lead to the temperature dependence of the effective spin-spin interaction constant.

In the clearest form this circumstance is manifested in works [6,16], where the decorated models of binary solutions, isomorphic to the standard Ising model, are constructed. Here the transformation to the standard Ising Hamiltonian is accompanied by the appearance of the generalized temperature, leading to the upper and lower critical points. In this approach the ideology of H bonds is not used, however, the introduction of nontrivial lattice structures in initial models can be justified only at switching on strongly anisotropic interactions, in particular H bonds.

Unfortunately, in all such approaches the cooperative character of H-bond network was not manifested explicitly.

In this paper we focus our attention on the quasithermodynamic nature of the temperature dependence of the effective ‘‘spin-spin’’ interaction constant in the Hamiltonians of Walker-Vause type intended to describe the phase transition in binary and quasiternary solutions with strong H bonds between molecules of different kinds. The H-bond network is considered as a subsystem, the behavior of which can be described in the thermodynamic terms. In particular, the existence of smeared phase transition in it may give rise to the nonmonotonic temperature dependence of the effective spin-spin interaction constant.

The work is organized as follows. In Sec. I the quasithermodynamic description of the H-bond network in the systems with the Hamiltonian of Walker-Vause type is given. The analysis of possible types of the phase diagrams is presented in Sec. II. The modeling of the effective spin-spin interaction constant within such a description of H-bond subsystem is carried out in Sec. III. The influence of small quantities of the third components is the object of Sec. IV. In the Appendixes we consider (1) the mean-field approximation for the free energy of the Ising model and the definition of the effective ‘‘spin-spin’’ interaction; (2) the electrostatic energy of an admixture particle, and (3) the fluctuation multipole interaction of the admixture particles.

I. TEMPERATURE DEPENDENCE OF THE EFFECTIVE INTERACTION CONSTANT IN THE GENERALIZED ISING MODEL

The Ising magnet is the simplest model system, in which the critical point takes place. For the Hamiltonian

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$$H_I=\sum_{\langle i,j\rangle} J(1-S_iS_j)-\sum_i^N h\,S_i\,,\quad J>0, \tag{1}$$

where S_i are random variables taking the values ± 1, the summation is carried out only on the nearest neighbors. The equation of state (EOS) in the mean-field approximation has the structure

$$\langle S_i\rangle=\tanh\left(\frac{\tilde J}{T}\langle S_i\rangle+h\right), \tag{2}$$

where

$$\tilde J=\tilde J(\mathbf{q})|_{\mathbf{q}=0}=z\,J,$$

$\tilde J(\mathbf{q})$ is the Fourier image of the spin-spin interaction on a lattice, z is the number of the nearest neighbors, and the Boltzmann constant $k_B=1$. From Eq. (2) it follows that the critical point of the Ising magnet is determined by the equation

$$\frac{\tilde J}{T_c}=1. \tag{3}$$

In such a system only one critical point is possible. The system is ordered only at $T<T_c$ ($\langle S\rangle\neq 0$) and completely disordered ($\langle S\rangle=0$) at $T>T_c$.

As is well known (see, e.g., Ref. [17]), the demixing transition in a binary mixture is isomorphic to ferromagnetic-paramagnetic one for the Ising model. However, because of more complex interparticle interaction the corresponding "spin-spin" interaction depends on the temperature, pressure, and difference of the chemical potentials for the components. As a result more than one critical point can be expected. If the effective spin-spin interaction constant of the corresponding Ising model depends on the temperature, the critical point is determined by the equation

$$T_c=\tilde J_{eff}(T_c). \tag{4}$$

The temperature dependence $\tilde J_{eff}$ appears in models more complex in comparison with Eq. (1). The models developed in Refs. [9] and [15] can serve as characteristic examples of such an approach:

$$J\to J_{ij}(\sigma)=J_{i\,j}+J_H\,\delta_{\sigma_i,\sigma_j} \tag{5}$$

[9] and

$$J\to J_{ij}(\sigma)=J+J_H\delta_{\sigma_i,\,1}\,\delta_{\sigma_j,1}. \tag{6}$$

[15]. The variables σ_i are the internal Potts variables and for each site i can assign q values $n=1,\dots,q$ independently. They are used to model q internal degrees of freedom of a molecule.

It is easy to see that the model (5) corresponds to the isotropic H bond, while Eq. (6) singles out one of the (directional) states. Because of the trivial identity

$$\delta_{\sigma_i,\sigma_j}=\sum_{k=1}^{q}\delta_{\sigma_i,\,k}\,\delta_{k,\,\sigma_j}$$

both these models can be considered as different limiting cases of the anisotropic model:

$$J\to J_{ij}(\sigma)=J+J_H\sum_{k=1}^{q}p_k\delta_{\sigma_i,k}\delta_{k,\sigma_j},\quad \sum_{k=1}^{q}p_k=1, \tag{7}$$

where the parameter p_k can be considered as the weight of kth H-bond forming state of a molecule. The constant J is the isotropic part of the interaction of van der Waals type. We assume that $J>0$, which corresponds to the following relation between the constants of intermolecular interaction [18]:

$$J_{AB}>\tfrac{1}{2}(J_{AA}+J_{BB}).$$

Note that in accordance with Eq. (1) only the "residual" part of the interaction between the molecules of A and B species is taken into account. In other words, the influence of the H bonds between the molecules of the same type on the demixing is ignored. To get the reentrant behavior in models of type Eq. (1) the interaction constant J_H should take the negative values. We expect that $|J_H|/T_m\simeq 1$, where T_m is the thermal energy at the melting point, although for H bond itself $J_H^{AA}/T_m\simeq 4-5$. Analogously, the corresponding contribution to the entropy s_H per H bond satisfies the inequality

$$s_H\lesssim 1. \tag{8}$$

In this case in mean-field approximation the excessive internal energy of a binary mixture can be written in the form

$$E=N\,c(1-c)\tilde J_{eff},\quad \tilde J_{eff}>0, \tag{9}$$

where c is the concentration of one of the components.

In the mean-field approximation with respect to spin variables S_i all such models based on the introduction of the internal σ variables lead to the EOS:

$$x=\frac{\langle\sinh[\beta\tilde J(\sigma)x+\beta\,h]\rangle_\sigma}{\langle\cosh[\beta\tilde J(\sigma)x+\beta\,h]\rangle_\sigma}, \tag{10}$$

where $x=\langle S_i\rangle$ and $J(\sigma)$ is the energy of "spin-spin," which explicitly depends on the "internal" (Potts-like) variables like in Eq. (7). The angular brackets

$$\langle\cdots\rangle_\sigma=\frac{\sum_\sigma\ \dots\exp[-\beta\tilde J(\sigma)]}{\sum_\sigma\ \exp[-\beta\tilde J(\sigma)]}$$

denote the average over internal degrees of freedom, which are considered independent of S_i. Here we assume that the introduction of the mean-field approximation for the spin variables S_i does not change the part of interaction connected with σ variables.

The situation here is rather similar to that in spin glasses, where the interaction energy J_{ij} is considered as a random variable over the configuration space [19]. So, the influence of the H-bond network cannot be neglected in consideration of glassy states of liquids such as water, glycerin, etc [20]. However, unlike the spin glasses, the characteristic spatial-time scales for variables describing the H-bond network in binary solutions are much shorter in comparison with those for spin variables. It means that 1) the averaging on internal variables can be performed independently. This circumstance allows us to introduce by the definition the effective "spin-spin" interaction energy $\widetilde{J}_{eff}$ (see also Appendix B):

$$\widetilde{J}_{eff}(T)=\langle\widetilde{J}(\sigma)\rangle_{\sigma}=z\,J+z_{H}(T)J_{H}, \tag{11}$$

where $z_H(T)$ is the average number of H bonds per molecule:

$$z_{H}(T)=\left\langle\sum_{j,k=1}^{q}p_{k}\delta_{\sigma_{i},k}\delta_{k,\,\sigma_{j}}\right\rangle_{\sigma}<z. \tag{12}$$

The residual energy and the entropy come from the internal degrees of freedom σ_i. To reduce analytical difficulties we use the mean-field approximation for the σ variables also (see, e.g., Ref. [21]).

If the mean-field approximation for the internal variables σ is used for Eq. (12), we can write

$$z_{H}(T)=z\sum_{k=1}^{q}p_{k}y_{k}^{2}, \tag{13}$$

where

$$y_{k}=\langle\delta_{\sigma,k}\rangle_{\sigma}\leqslant 1. \tag{14}$$

It is clear that Eq. (13) is equivalent to neglecting the correlations between the different internal states of the molecules.

To guarantee the isomorphism with the standard Ising model the value of $\widetilde{J}_{eff}(T)$ should be positive. In principle, this does not exclude the possibility $|J_H|>J$ for the bare constant of H-bond interaction.

From the definition it is clear that y_k is nothing but the probability for the molecule to be in kth internal state. Note that according to its definition Eq. (11), in the mean-field approximation $\widetilde{J}_{eff}$ can be treated as the internal energy for the subsystem of H bonds.

In general, the variables x and y are determined by the system of two nonlinear equations. To get the qualitative picture we will consider the vicinity of the critical points where $x=0$ and $h=0$. There we denote the values of y_k as $y_k^{(0)}$. In such a state all thermodynamic variables depend on the whole set $\{y_k^{(0)}\}$,

$$y_{k}^{(0)}=\frac{\sum_{\sigma}\delta_{\sigma,k}\exp[-\beta J(\sigma;\{y_{k}^{(0)}\})]}{Z_{\sigma}},$$

$$Z_{\sigma}=\sum_{\sigma}\exp[-\beta J(\sigma;\{y_{k}^{(0)}\})]. \tag{15}$$

The closed loop coexistence curves appear when the solution of Eq. (4) bifurcates. Namely, besides the Ising-like solution with small $y^{(0)}\sim 1/q, T^{u}\simeq 1q\gg 1$, either one or two others $y^{(u)}(T)\geqslant y^{(l)}(T)$ appear, thus giving rise to the reentrant behavior. Sure, the mean-field bifurcation of state for the internal degrees of freedom described above in terms of $y(T)$ should be corrected via taking into account the fluctuations. Nevertheless, we will suppose that the topology of the phase diagram remains unchanged. Besides, as has been said above, the dependence of the interaction constant J on the internal variables σ regardless of the specific model leads to the temperature dependence of $\widetilde{J}_{eff}$. The general condition on this dependence for the appearance of the reentrant behavior will be derived below.

As follows from above, the H-bond network can be treated as a subsystem, which is described by thermodynamic methods. As a result, the change of H-bond ordering in some solutions can be considered as a smeared phase transition or a succession of such transitions. A similar situation is characteristic for magnetic media. There the interaction of spins with the translational degrees of freedom is often negligibly small and therefore a sharp paramagnetic-ferromagnetic phase transition is possible. As it follows from above, the continuity of $\widetilde{J}_{eff}(T)$ with respect to the temperature is the natural physical demand imposed on it.

The existence of high- and low-density supercooled water with different character of H-bond ordering in such metastable phases is a clear demonstration of the smeared phase transition in the subsystem of H bonds. Besides, the anomalies of density and compressibility in normal water are also the results of macroscopic transformations of H-bond network. Thus we can introduce the effective mean field, with the energy $\widetilde{J}_{eff}$ depending on the temperature (see Appendix B). This reflects the smeared character of the phase transition in the H-bond system.

II. POSSIBLE TYPES OF PHASE DIAGRAMS

From the general point of view $\widetilde{J}_{eff}(T)$, introduced above, should have natural low- and high-temperature asymptotes:

$$\beta\widetilde{J}_{eff}(T)\propto\frac{1}{T}\quad\text{if}\quad T\rightarrow 0\quad\text{or}\quad T\rightarrow\infty, \tag{16}$$

i.e., the only *a priori* physical constraint imposed on $\widetilde{J}_{eff}$ is its boundedness. In accordance with our arguments, the noticeable temperature dependence of $\widetilde{J}_{eff}$ takes place only near the points of smeared phase transition in the subsystem of H-bonds. For the simplicity we assume that there is only one point of such a transition. In such a case more than one critical point may appear if the value $\widetilde{J}_{eff}$ changes significantly enough with the temperature due to the reconstruction of order in the subsystem of H bonds. If there is an additional parameter of state λ, e.g., pressure or concentration of the admixture, the value of $\widetilde{J}_{eff}$ depends on this parameter too.

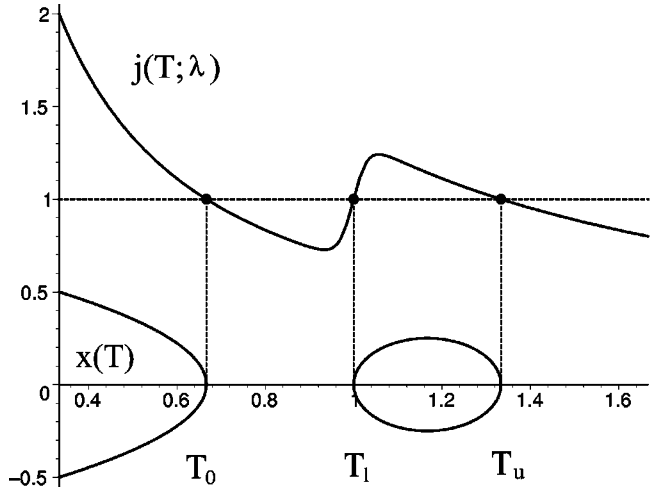

FIG. 1. Phase diagram for the system with closed loop binodal and corresponding temperature behavior of $\beta\tilde{J}_{eff}$

Let T_a and T_b be the points of local minimum and maximum of the function

$$j(T;\lambda)=\frac{\tilde{J}_{eff}(T;\lambda)}{T} \tag{17}$$

at some fixed λ (see Fig. 1), where λ stands for the set of additional parameters of state (pressure, chemical potential, etc.).

From Fig. 1 and the condition given by Eq. (4) it is clear that there exist different types of phase diagrams, with and without closed loop. Depending on the number of roots $(\leqslant 3)$ of Eq. (4), the phase diagram is the "superposition" of the closed immiscibility curve with upper and lower critical points and a curve with upper critical point only.

There are the following characteristic situations:

$$\begin{gathered} j(T_a;\lambda)>1 \quad \text{or} \quad j(T_b;\lambda)<1, \\ j(T_a;\lambda)<1<j(T_b;\lambda), \\ j(T_a;\lambda)=1 \quad \text{or} \quad j(T_b;\lambda)=1. \end{gathered} \tag{18}$$

In the first case only one root of Eq. (4) exists. This is the only ("upper") critical point of a system. In the second case Eq. (4) has three solutions:

$$T_0<T_l<T_u$$

corresponding to two upper T_0, T_u and one lower T_l critical points. The coexistence curve of a system consists of two parts: the closed loop with upper and lower critical points $T_l<T_u$ and the separated curve with the upper critical point at T_0 (see Fig. 1). Namely, this type of phase diagram corresponds to the models investigated in Refs. [15,16].

Merging the roots T_l, T_u of Eq. (4) at T_b, the equality $\tilde{J}_{eff}(T_b)/T_b=1$ means that the closed loop disappears and the DCP appears. The degeneracy of the roots T_0, T_l at T_a, when $\tilde{J}_{eff}(T_a)/T_a=1$, leads to the so called critical double point (hour-glass form of the phase equilibrium line) observed in binary gases such as He+Ne, Ne+Xe, etc. [1]

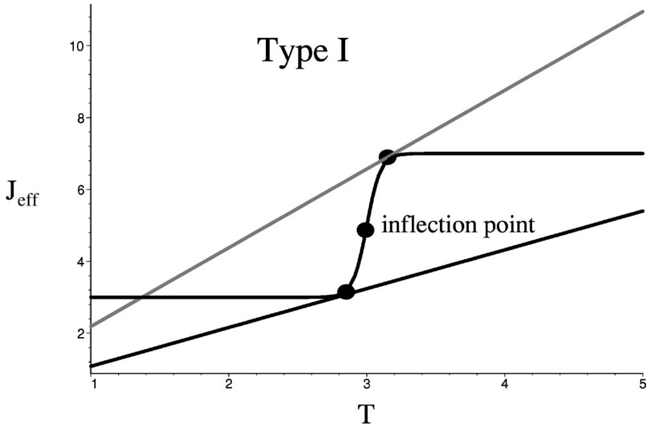

FIG. 2. The temperature behavior of $\tilde{J}_{eff}(T)$, corresponding to Fig. 1.

It is possible that because of the specific thermodynamic properties one or both of the left and right points (T_0 and T_u in Fig. 1) are out of the stability region of the considered equilibrium phases so that the corresponding part of the phase diagram with corresponding phases is inaccessible.

Within the general framework of singularity theory [22–24] the described situations correspond to the statement that in a one-parameter family of functions (17) only A_3 catastrophe, with respect to the variable *T*, is possible (see Fig. 1). This is equivalent to the condition that the equation

$$\frac{d}{dT}\left(\frac{\tilde{J}_{eff}}{T}\right)=0 \quad \text{or} \quad T\frac{d\tilde{J}_{eff}}{dT}-\tilde{J}_{eff}(T)=0 \tag{19}$$

has no more than two solutions.

From a simple geometric interpretation of Eq. (19) and natural constraint of boundedness of $\tilde{J}_{eff}$ it follows that the criterion for two roots of Eq. (19) to appear is the existence of the inflection point T_{infl} for $\tilde{J}_{eff}(T)$. There can be three types for the temperature behavior of $z_H(T)$, which lead qualitatively to the same $j(T;\lambda)$. They are shown in Fig. 2 and Fig. 3. Note that the behavior for $\tilde{J}_{eff}(T)$ shown in Fig. 2 is a consistent with the natural assumption that $z_H(T)$ is a monotonically decreasing function of the temperature, when other effects important for the H-bond network structure such as thermal expansion are not taken into account. The change in structure leading to the appearance of the reentrant behavior should be attributed to the increase in the average number of H bonds $z_H(T)$ with decrease in temperature $T<T^*$. This is exactly in agreement with the picture where the upper critical point is identified with that of van der Waals type, while the lower critical point, where $z_H(T_u)<z_H(T_l)$, is due to H-bond network formation because of anisotropic interactions. The types II and III shown in Fig. 3 correspond to the nonmonotonous temperature behavior of $z_H(T)$. It is interesting to develop the models in which such possibilities are realized.

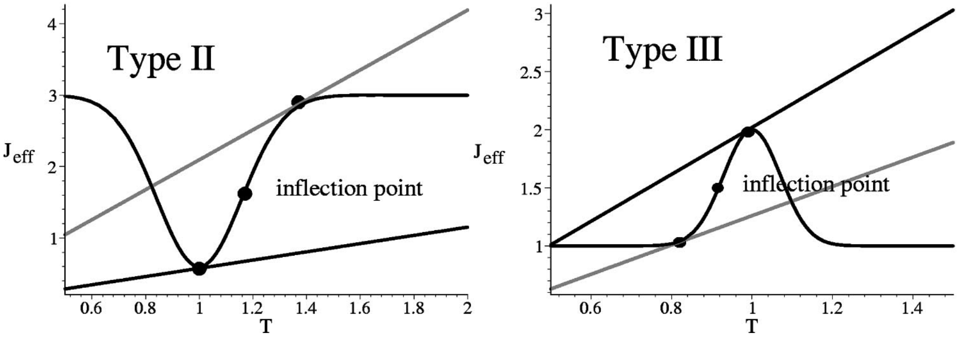

FIG. 3. Two other types of temperature behavior of $J_{eff}(T)$ leading to qualitatively same behavior $j(T;\lambda)$ shown in Fig. 1.

It is instructive to consider the behavior of the excessive entropy, corresponding to $\tilde{J}_{eff}$ depending on the temperature. The schematic temperature dependence of the entropy is depicted on Fig. 4. Note the characteristic S-shaped temperature dependence of the excess entropy, i.e., starting from upper critical point the immiscible phase is more ordered than the miscible one, until order parameter reaches its maximum. Here the situation resembles that in a superconductor-conductor transition, where the equality of the entropies for the normal and superconductor states takes its place at the critical point itself and at $T=0$ K, when the order parameter takes maximum value (see, e.g., Ref. [25]). The analog of the point $T=0$ K in our case is the temperature T_M, which corresponds to the maximum value of an order parameter, e.g., concentration of one of the components. In other words, in such a point the excess free energy is equal to the excess internal energy.

Below the temperature T_M the excess entropy becomes positive, i.e., the immiscible state becomes relatively disordered but is still stable because of the energetic effect of the interaction. Further below, the entropy vanishes at the lower critical point. It is clear that such S-shape behavior of the excess entropy is in full agreement with the approach based on Landau-Ginzburg effective functional [1,21].

The result obtained has more simple formulation in variable, which is Legendre conjugated to T,

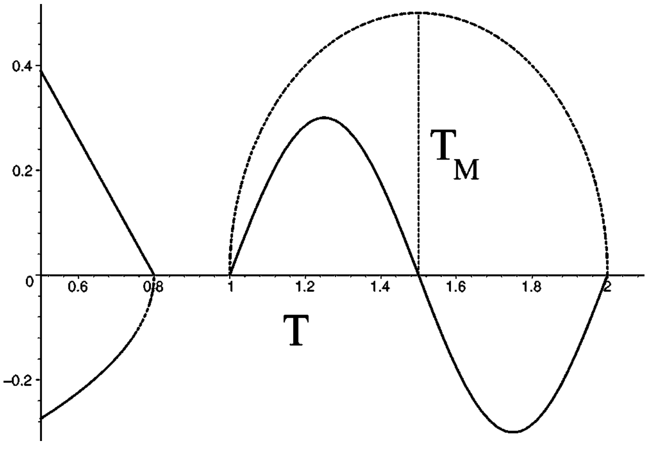

FIG. 4. Qualitative temperature behavior of the excessive entropy S (solid curve) of the mixture with the closed immiscibility loop. The dashed curve is the schematic dependence of the order parameter x.

$$p=\frac{d\tilde{J}_{eff}}{dT}. \tag{20}$$

In this representation Eq. (19) takes the form

$$\tilde{J}^{(L)}_{eff}(p)=0, \tag{21}$$

where

$$\tilde{J}^{(L)}_{eff}(p)=pT-\tilde{J}_{eff} \tag{22}$$

is the Legendre transform (see, e.g., Ref. [26]) of $\tilde{J}_{eff}$. Note that the existence of inflection points for the function results in existence of the cuspidal (return) points for the graph of its Legendre transform (see, e.g., Ref. [26]). In such a sense necessary and sufficient condition for the reentrant behavior to occur is the existence of solutions of Eq. (21) with the cusp singularity. The special points of other types such as critical inflection point (CIP) or quadruple critical point (QCP) according to terminology of works [1,27] are possible for the systems with at least two thermodynamic fields, in particular in ternary solutions [27]. The catastrophe theory classification is as follows: (1) CIP corresponds to the germ of A_3 catastrophe for the $j(T;\lambda)$; (2) QCP is the germ of A_4 catastrophe for the $j(T;\lambda)$.

III. THE THERMODYNAMIC APPROACH FOR THE MODELING OF $\tilde{J}_{eff}$

In the preceding section we emphasized that the H-bond network may be considered as an almost independent subsystem, the properties of which can be described by thermodynamic methods. The corresponding thermodynamic variables are naturally named by the structural functions. The simplest and the most important are (1) the average number of H-bonds per molecule $z_H(T,P)$ and the parameter $t_H(T,P)$ describing the bending of H-bond network. In the case of pure water this parameter is known as the tetrahedricity parameter, which measures the deviation from the ideal geometric H-bond network. These parameters can be found with the help of the numerical simulations (see Ref. [28]) or within the special statistical methods (see, e.g., Refs. [29,30]).

The arbitrary thermodynamic function $Q(T,P)$ of the H-bond network can be expanded in a series with respect to structural functions (like the Hilbert's principle in the theory of invariants [31]):

$$Q(T,P)=\lambda_1 z_H(T,P)+\lambda_2 t_H(T,P)+o(z_H,t_H). \tag{23}$$

The successful application of such an approach for the description of the anomalous behavior of the density and the dielectric permittivity of pure water was proposed in Ref. [32]. The formalism of structural functions allows to understand adequately the difference between low- and high-density water observed under deep enough supercooling (see Ref. [33]).

From this point of view the contribution $\tilde{J}_H(T,P)$ of H bonds into $\tilde{J}_{eff}$ can be represented in the form

$$\tilde{J}_H(T,P) = -\alpha_1 z_H + \alpha_2 t_H + \cdots, \quad \alpha_1, \alpha_2 > 0. \tag{24}$$

The coefficient α_1 is close to $|J_H|$ used above in the simplified lattice approach where the deformations of the lattice were neglected. Obviously, the functions z_H and t_H have opposite temperature dependencies.

Near some temperature T_* the structural function z_H can diminish sharply enough, which corresponds to the smeared phase transition in the subsystem of H bonds. As a result, the behavior of $\tilde{J}_{eff}(T)$ in the vicinity of T_* is of sigmoidal character (see Fig. 2) and can stimulate the demixing in binary solution.

The formalism of structural functions allows also to establish the connection between the variations of $\tilde{J}_{eff}$ and the dielectric permittivity ϵ of a system. Indeed, ϵ can be represented in the form

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} n[(1-x)\alpha_{eff}^{(1)} + x\alpha_{eff}^{(2)}], \tag{25}$$

where n is the density of molecules and $\alpha_{eff}^{(i)}$, $i=1,2$ are the effective molecular polarizabilities of the components. In general, $\alpha_{eff}^{(i)}$ includes the electronic and dipole parts:

$$\alpha_{eff}^{(i)} = \alpha_e^{(i)} + \alpha_d^{(i)}.$$

The first term is close to the electronic polarizability of an isolated molecule and therefore its temperature and concentration dependence is weak. The second term has the structure

$$\alpha_d^{(i)} = \frac{d_i^2}{3k_BT}$$

in which the effective dipole moment d_i within our approach should be represented as

$$d_i = d_i^{(0)}(1 + r_1 z_H + r_2 t_H + \cdots).$$

It means that the nonmonotonic behavior of the structural functions should become apparent in corresponding peculiarities of the dielectric permittivity.

IV. PERTURBATIONS OF THE BINARY MIXTURE PARAMETERS OF THE PHASE EQUILIBRIUM

In recent years a lot of studies have been carried out to analyze the influence of different kinds of perturbations on the phase diagram of the binary mixtures with H bonding. These perturbations include changing the external pressure [2], variance of isotopic composition [34], and small addition of the third component [4], in particular, electrolyte [35–37]. Experimentally it was noted that the shifts of the upper and lower critical points with variation of either pressure or third component addition are almost the same at least qualitatively [38]. Below we discuss the influence of these perturbations within the approach presented in the previous sections.

The thermodynamic potential of a binary system intrinsically depends on three parameters of state. Two of them are ‘‘external fields‘‘ the temperature T and pressure P, another field is the difference of the chemical potentials of the components $\mu = \mu_1 - \mu_2$ [39]. Then the Gibbs free energy is

$$dg = -s\, dT + v\, dP + \mu\, dx_1, \quad \mu = \mu_1 - \mu_2, \tag{26}$$

where $x_i = N_i/N$ is the molar fraction of the components and s, v, and μ_i are the specific entropy, the volume, and chemical potentials correspondingly. We will use also the potential f conjugated to g:

$$f(T,P,\mu) = g(T,P,x) - x_1\mu,$$

which according to Gibbs-Duhem identity is the chemical potential μ_2 of another component.

Further we fix the type of the component chosen in Eq. (26) and will omit the subscript. The corresponding critical points (T_c, P_c, x_c) are determined by the conditions [39]

$$\left.\frac{\partial^2 g}{\partial x^2}\right|_{T,P} = 0, \quad \left.\frac{\partial^3 g}{\partial x^3}\right|_{T,P} = 0. \tag{27}$$

The thermodynamic fields T and P drive the equilibrium phase separation in the two phase region. From the thermodynamic point of view the conditions (27) are analogous to that for the liquid-vapor critical point. This is the basis for the isomorphism between these systems and simple liquids. The concentration x serves as the initial order parameter for the demixing transition. Its conjugated field is μ. According to the catastrophe theory [22–24] with the help of the smooth transformation $\eta \rightarrow \psi$,

$$\psi = \eta + \gamma_1(P,T)\, \eta + \gamma_2(P,T)\, \eta^2 + \cdots, \tag{28}$$

where $\eta = x - x_c$, the Landau thermodynamic potential g near the critical point is reduced to the canonical form

$$\tilde{g}(\psi; T,P) = \frac{a_4(T,P,\mu)}{4}\psi^4 + \frac{a_2(T,P,\mu)}{2}\psi^2 + a_1(T,P,\mu)\psi. \tag{29}$$

The explicit expressions for a_i and γ_i can be easily obtained (see, e.g., Ref. [23]). The treatment of the isomorphism principle in terms of the canonical forms was developed in Ref. [21] for the specific case of the systems with the DCP. It should be noted that the theory of singularities of smooth mappings [24] admits reduction to the canonical form (29) only locally, in the vicinity of the critical point, where the series (28) converges. The approach, developed in Ref. [40], works directly with the Hamiltonian and allows to construct the transformation (28) nonperturbatively.

The dependence of the coefficients a_1 and a_2 of the canonical form (29) on the state variables determines the topology of the phase diagram. Note that such a dependence in general is nonlinear even in the mean-field approximation because of the nonlinearity of the transformation $x \to \psi$. Due to this transformation the isomorphism between Ising model and the critical behavior of the binary mixture is established [41]. In the vicinity of the critical point, a_1 and a_2 can be approximated by simple linear functions of the initial thermodynamic fields [42].

The inclusion of fluctuation effects can be done with the help of the renormalization group method.

The influence of small admixtures within the method of effective “spin-spin“ interaction can be done with the help of thermodynamic perturbation theory [39]. Within the approach proposed above, such perturbations modify the value of $\tilde{J}_{eff}$ causing its dependence on the concentration c of the admixture according to

$$f_{\mathrm{CW}}(T,P,\tilde{J}_{eff}+\delta\tilde{J}_{eff})=f_{\mathrm{CW}}(T,P,\tilde{J}_{eff})+\varphi(T,P,x,c), \tag{30}$$

where φ is the excess thermodynamic potential caused by the small addition of the third component. In other words, φ is the part of the thermodynamic potential Φ of an admixture

$$\Phi(T,P,x,c)=\Phi(T_c,P_c,x_c,c)+\varphi(T,P,\eta,c), \tag{31}$$

which depends on the order parameter. The first term in Eq. (31) is included into regular part of the thermodynamic potential of the system.

The corresponding thermodynamic potential f_{CW} of the equivalent Ising model is as follows (see Appendix B):

$$f_{\mathrm{CW}}(T,h;\tilde{J}_{eff})=-\frac{\tilde{J}_{eff}}{2}x^2+T\left[x\,\mathrm{arctanh}(x)+\frac{1}{2}\ln(1-x^2)\right]-x\,h, \tag{32}$$

where $x(T,h;\tilde{J}_{eff})$ is determined by the Curie-Weiss EOS (B3) in which the conjugated field h is the difference of the chemical potentials of the phases.

Thus the change of the phase diagram of the binary mixture is interpreted as the corresponding variation of $\tilde{J}_{eff}$:

$$\delta\tilde{J}_{eff}=\frac{\varphi}{\dfrac{\delta f}{\delta\tilde{J}_{eff}}}. \tag{33}$$

Note that due to the definition $\varphi=0$ in disordered phase, where $x=0$. Taking into account the equation for binodal

$$x^2=3(\beta\tilde{J}_{eff}-1)+o(\beta\tilde{J}_{eff}-1) \tag{34}$$

and the expansion for the excessive free energy:

$$f=\tfrac{1}{2}(1-\beta\tilde{J}_{eff})x^2+\tfrac{1}{12}x^4+o(x^4), \tag{35}$$

for the derivative $\delta f/\delta\tilde{J}_{eff}$ we get:

$$\frac{\delta f}{\delta\tilde{J}_{eff}}=\frac{3}{2}(1-\beta\tilde{J}_{eff})+o(\beta\tilde{J}_{eff}-1)<0, \quad \text{for} \quad \beta\tilde{J}_{eff}>1. \tag{36}$$

Thus the sign of $\delta\tilde{J}_{eff}$ is opposite to that for φ. Therefore in accordance with Eq. (4) (see also Fig. 1) the change of the phase equilibrium is determined by the following:

$$\beta(\tilde{J}_{eff}+\delta\tilde{J}_{eff})=1, \tag{37}$$

and if $\delta\tilde{J}_{eff}>0$ the closed immiscibility loop will expand or even may appear at sufficiently big value of $\delta\tilde{J}_{eff}$, while if $\delta\tilde{J}_{eff}<0$ the loop will shrink or even may disappear.

A. Influence of electrolyte admixture on the phase equilibrium of the H-bond mixtures

The influence of small addition of the electrolyte in Debye-Huckel approximation can be described as

$$f(T,h,c)=f_{\mathrm{CW}}(T,h)+\varphi_{\mathrm{DH}}(T,P,c), \tag{38}$$

where

$$\varphi_{\mathrm{DH}}(T,P,c)=\frac{(P\,T)^{1/2}}{24\pi}(\Gamma^3-\Gamma_c^3), \quad \Gamma^2=\frac{4\,\pi\sum_a e^2\,z_a^2 c_a}{\epsilon T},$$

ϵ is the dielectric permittivity of a binary mixture, c_a is the concentration of ions of ath kind, and z_a is their valency. Note that due to symmetry with respect to the type of the components the value of μ does not change because of the equal shifts of μ_1 and μ_2. It is clear also that due to continuity of the thermodynamic potential the value Γ is the same in both phases since it determines the thermodynamic potentials for the electrolyte [39].

The difference $\Gamma(x)-\Gamma_c$, which depends on the concentration x through the dielectric permittivity (see Ref. [43]), may be either of the same sign or has different ones in the vicinity of the upper and lower critical points. In the first case, in accordance with Eq. 33 the coexistence loop either shrinks or expands almost symmetrically with respect to the upper and lower critical points. In the second case the upper and lower critical points shift in the same direction, though these displacements may be different.

B. Influence of hydrophobic admixture molecules of type CCl_4

The addition of CCl_4 molecules to the guaiacol-glycerin mixture leads to the appearance of the closed loop of immiscibility at very small concentrations [4]. It is naturally explained by the breaking of the H-bond network and as a sequence the increase of $\tilde{J}_{eff}$ so that $\tilde{J}_{eff}(T_b)>1$ and the closed loop appears (see Fig. 1).

The same effect is observed if water molecules are added, though their molar concentration is approximately four times greater in comparison with the case of CCl_4 [4].

The admixture molecule CCl_4 produces significant distortions in H-bond network in its vicinity. The breaking of H bonds and their bending are connected with considerable energy. Therefore the solubility of such molecules is very small. Besides, the average energy per H bond diminishes, which leads to noticeable variation of the phase diagram. Let us consider the influence of such an admixture in more detail.

We assume that H bonds break and are strongly distorted only in the monomolecular layer around CCl_4. As follows from simulations [44] and the spectroscopy measurements [45], a similar behavior of H-bond network is observed near the ions which is order breaker (chaotropes) in a dilute aqueous electrolyte solution. Although comparatively, the influence of a molecule CCl_4 due to its electroneutrality is much weaker. The breaking and bending of H bonds in the close neighborhood of CCl_4 generate the appearance of the spontaneous dipole moment, which can be attributed to an admixture molecule. As a result the interaction between admixture molecules renormalizes strongly (see Appendix C).

The increment of the free energy caused by the dissolving of CCL_4 molecules can be represented as following:

$$\varphi=\varphi_0+c_a\psi_1+\tfrac{1}{2}c_a^2\psi_2+\cdots, \tag{39}$$

where c_a is the concentration of the admixture molecules, φ_0 correspond to the ideal solution approximation,

$$\psi_1=\psi_H+\psi_d$$

is the one-particle contribution, which consists of two terms. The first term ψ_H corresponds to the breaking and bending of the H bond, the second one ψ_d describes the formation of the electric field around the admixture molecule. The pair contribution coefficient ψ_2 for a dilute solution is equal to the energy of the dipole-dipole interaction. The contribution ψ_H can be approximated as

$$\psi_H\sim|J_H|\zeta, \tag{40}$$

where ζ is the number of broken H bonds in the surface layer.

To estimate the value of ψ_d we use the double layer approximation. The corresponding result is derived in Appendix A:

$$\psi_d=2\,\pi r_a\frac{\epsilon_1(x)\epsilon_2}{2\epsilon_1(x)+\epsilon_2}\sum_{m=0,\pm1}\langle|\tau_{1,m}|^2\rangle, \tag{41}$$

where $\epsilon_1(x)$ is the dielectric permittivity of a binary solution, ϵ_2 is the effective dielectric permittivity of a cavity, formed by the admixture molecule, and r_a is the radius of a cavity similar to Kirkwood's consideration of zwitterions [46]. It is not difficult to see that

$$\sum_{m=0,\pm1}\langle|\tau_{1,m}|^2\rangle=\frac{\langle\mathbf{d}_s^2\rangle}{r_a^4}, \tag{42}$$

therefore

$$\psi_d=2\pi\frac{\epsilon_1(x)\epsilon_2}{2\epsilon_1(x)+\epsilon_2}\frac{\langle\mathbf{d}_s^2\rangle}{r_a^3}. \tag{43}$$

The solubilities of admixture molecules CCl_4 in pure guaiacol-glycerin are different since the parameters of H-bond networks of these substances differ essentially. The solubility of CCl_4 in guaiacol is greater. Due to this the admixture molecules of CCl_4 stimulate the demixing in the solution discussed.

More formally, the demixing can be described in the following way. In accordance with our assumptions, the solution of the third component changes the internal energy of the system by the value

$$\Delta E=N_a\zeta(J_1-J_H),\quad J_1=\psi_d/\zeta, \tag{44}$$

where N_a is the number of CCl_4 molecules. The number of broken H bonds in the neighborhood of an admixture particle is

$$\zeta=n\,zv_Lx(1-x), \tag{45}$$

where v_L is the volume of the monomolecular layer,

$$v_L\approx4\pi r_a^2r_s,$$

r_a is the radius of an admixture particle, and r_s is the average radius of a molecule in a binary mixture. From Eq. (9) and Eqs. (44) and (45) it follows that the renormalized value of $\tilde{J}_{eff}$ is

$$\tilde{J}_{eff}^{(r)}=\tilde{J}_{eff}+v_Ln_a(J_1-J_H). \tag{46}$$

Let us estimate the relation between ψ_1 and J_H. Assuming that the dipole moments of molecules in a surface layer are not correlated, we may use the estimate

$$\langle\mathbf{d}_s^2\rangle\sim\zeta\langle\mathbf{d}_H^2\rangle,$$

where d_H is the variation of the dipole moment due to the breaking or formation of a H bond. By order of magnitude

$$|d_H|\leqslant\frac{d_w}{4},$$

where $d_w\simeq1.7D$ is the dipole moment of an isolated water molecule [47].

To get the estimate for ψ_d it seems to be justified to put $r_a\sim5$ Å and $\epsilon_1,\ \epsilon_2\sim1$, which corresponds to the values of the dielectric permittivity on the frequency $\omega_H\sim1/\tau_H$, where $\tau_H\sim10^{-12}$ s is the typical lifetime of H-bond [47]. Then

$$\psi_d\leqslant k_BT_r\zeta.$$

Since, in accordance with Sec. I, $|J_H|\leqslant k_BT_r$, where T_r is the room temperature, we obtain the estimate

$$\frac{\psi_d+\psi_H}{k_BT}\simeq1-2\zeta. \tag{47}$$

The concentration of admixture molecules is determined by the formula [39]:

$$c_a = \frac{P}{n_s k_B T} \exp\left(-\frac{\psi_d + \psi_H}{k_B T} \right),$$

where P is the pressure of gas CCl_4 contacting the solution, n_s is density of the solution. In accordance with Eq. (45) $\zeta \sim 3-6$, if $r_s = 3$ and $z = 2-4$. At $P = 1$ bar the concentration of admixture molecule

$$c_a \leqslant 10^{-4} - 10^{-3}$$

agrees with experimental values [4] and shows the self-consistency of our approach.

From here it follows that $J_1 - J_H > (\gg) 1$. Therefore the increase of $\tilde{J}_{eff}$ may lead to the phase separation of the homogeneous mixture. The physical mechanism of breaking the H-bond network under addition of water molecules differs from that for CCl_4. The formation of glycerin-water associates is energetically profitable. It means that the admixture water molecules will stimulate the microdemixing in the system. From this point of view the influence of water admixture is analogous to that for CCl_4, i.e., the effective spin-spin interaction constant of the binary solution becomes greater, though because of difference in geometric parameters to produce the same effect the concentration of water molecules is less than the corresponding concentration of CCl_4.

DISCUSSION

The main attention in this paper was paid to the nature of the DCP in binary solutions with H-bonds. The influence of H bonds is discussed in the framework of an Ising-like Hamiltonian with the spin-spin interaction, the value of which depends on the random internal variables characterizing the H-bond network. In particular the Potts variables may serve as the example. It is taken into account that the characteristic relaxation times in a H-bond network are essentially less in comparison with those for the spin subsystem. Due to this the spin-spin interaction in the Ising-like Hamiltonian should be determined by the averaged characteristics of the H-bond network. In other words the influence of H bonds is described with the help of the Ising Hamiltonian with the effective constant $\tilde{J}_{eff}$ depending on the temperature, pressure, and other external parameters of state via the corresponding dependence of the structural functions of H-bond network. To describe the properties of H-bond contribution $\tilde{J}_H(T)$ into $\tilde{J}_{eff}$ we apply the Hilbert's principle in accordance with which $\tilde{J}_H(T)$ can be expanded in a series with respect to the structural functions which form the complete basis for H-bond network mesoscopic description. Within the conception of such an effective Hamiltonian the behavior of the binary solution with a small admixture of the third component is possible. It was shown that the neutral admixture CCl_4 leads to the increase of $\tilde{J}_{eff}$ for the guayacol-glycerin solution because of the decrease of z_H. As a result the homogeneous solution becomes unstable and demixes. Thus the doubts about the role of H bonds stated in Ref. [4] are groundless. It was shown that the admixture of water stimulates the demixing also because water molecules are H bonded mainly with the glycerin molecules. The greater quantity of water molecules than that in case of CCl_4 is explained by more intensive breakage of H bonds by CCl_4.

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APPENDIX A: ELECTROSTATIC ENERGY OF A PARTICLE

In accordance with our assumption, the dipole moment of an admixture molecule is formed by the molecules of a solvent, which form a monomolecular layer around the admixture particle. Within the macroscopic electrodynamics the thickness of such a layer vanishes. Thus we come to a double layer with some power τ, which determines the work for passing the double layer. Inside and outside a particle, the potential of the electric field satisfies the Laplace equation

$$\Delta\varphi_1 = 0, \quad r > r_a,$$
$$\Delta\varphi_2 = 0, \quad r < r_a \tag{A1}$$

and the boundary conditions

$$\varphi_1 - \varphi_2 = 4\pi\tau(\mathbf{r}),$$
$$\epsilon_1 \frac{\partial\varphi_1}{\partial r} = \epsilon_2 \frac{\partial\varphi_2}{\partial r} \tag{A2}$$

at $r = r_a$.

It is not difficult to see that

$$\varphi_1 = 4\pi \sum_{l=0}^{\infty} \frac{l\epsilon_2}{(l+1)\epsilon_1 + \epsilon_2 l} \left(\frac{r_a}{r} \right)^{l+1} \tau_{l,m} Y_{l,m}(\theta,\varphi),$$
$$\varphi_2 = -4\pi \sum_{l=0}^{\infty} \frac{(l+1)\epsilon_1}{(l+1)\epsilon_1 + \epsilon_2 l} \left(\frac{r}{r_a} \right)^{l} \tau_{l,m} Y_{l,m}(\theta,\varphi), \tag{A3}$$

where $\tau_{l,m}$ are spherical components of the distribution $\tau(\theta,\phi)$:

$$\tau_{l,m} = \frac{1}{4\pi} \int \tau(\theta,\phi) Y^*_{l,m}(\theta,\varphi) d\Omega,$$

$$\frac{1}{4\pi} \int Y^*_{l,m}(\theta,\varphi) Y_{l',m'}(\theta,\varphi) d\Omega = \delta_{ll'} \delta_{mm'}$$

The electrostatic energy W of a particle is determined by the expression

$$W = \frac{1}{8\pi} \left(\int_{|r|>r_a} \epsilon_1 (\nabla\varphi_1)^2 dV + \int_{|r|<r_a} \epsilon_2 (\nabla\varphi_2)^2 dV \right), \tag{A4}$$

which can be rewritten in the form

$$W_d = -4\pi r_a^2 \epsilon_1 \oint \frac{\partial \varphi_1}{\partial r} \tau d\Omega. \tag{A5}$$

Substituting Eq. (A3) in Eq. (A5), we obtain

$$W_d = 2\pi r_a \frac{\epsilon_1 \epsilon_2}{2\epsilon_2 + \epsilon_1} \sum_{m=0,\pm 1} |\tau_{1,m}|^2 + \cdots. \tag{A6}$$

Explicit form of contributions of higher orders is also evident.

APPENDIX B: MEAN-FIELD APPROXIMATION FOR THE FREE ENERGY OF THE ISING MODEL AND THE EFFECTIVE "SPIN-SPIN" INTERACTION

Here we derive the expression (32) for the Helmholtz energy in the mean-field approximation. Let $x = \langle S \rangle$ be the magnetization. In the mean-field approximation the Hamiltonian (1) is reduced to the following:

$$H = -(h + \tilde{J}x) \sum_i S_i, \tag{B1}$$

and the free energy per particle of the system is

$$F_{\mathrm{mf}}(x;T,h) = -T \ln \cosh\left(\frac{\tilde{J}}{T} x + \frac{h}{T} \right). \tag{B2}$$

The parameter x is fixed by the self-consistency condition: $x = -\partial F_{\mathrm{mf}}/\partial h$, which leads to the classical Curie-Weiss EOS

$$x(T,h) = p_{\mathrm{CW}}(x;T,h), \tag{B3}$$

where

$$p_{\mathrm{CW}}(x;T,h) = \tanh\left(\frac{\tilde{J}_{eff}(T)}{T} x + \frac{h}{T} \right). \tag{B4}$$

The equivalent result may be obtained starting from the Landau potential $F_L(T,h,x)$ completed by the extremum condition $\partial F_L(T,h,x)/\partial x|_{T,h} = 0$.

Equations (B3) and (B4) give

$$h = -\tilde{J}x + T \,\mathrm{arctanh}(x), \tag{B5}$$

which defines $x(T,h)$ and leads to the following form of the Landau potential:

$$F_L(T,h,x) = -\frac{\tilde{J}}{2} x^2 + Tx \,\mathrm{arctanh}(x) + \frac{T}{2} \ln(1 - x^2) - xh. \tag{B6}$$

The thermodynamic potential $F(T,h)$ is simply expressed through the Landau potential:

$$F(T,h) = F_L(T,h,x(T,h)).$$

The introduction of other internal degrees of freedom like σ_i in the mean-field approximation leads only to the effective temperature dependence of $\tilde{J}$. Thus the expression (32) is justified.

The mean-field equation of state for the Ising-like models of H-bond mixture was obtained in Sec. I [see Eq. (10)]. Note that any approximate approach to the EOS is based on the condition of self-consistency: $x = p(x;T,h)$. In particular, the explicit form of p can be determined by Eq. (10). For the Curie-Weiss EOS it is given by Eq. (B4). Though the function p is determined within the specific model of type (10), nevertheless there are the following natural demands imposed on it: (1) $p(x=0;T,h=0)=0$, (2) $p(x;T,h) \leqslant 1$, (3) $p(x;T,h)$ is the monotonic function of x.

Because of these properties the relation between initial model and the corresponding Ising model with the effective "spin-spin" interaction $\tilde{J}_{eff}(T)$ can be defined as follows

$$p(x;T,h) = \tanh\left(\frac{\tilde{J}_{eff}(T,h)}{T} \tilde{x} + \frac{h}{T} \right). \tag{B7}$$

Equation (B7) defines the "magnetization" $\tilde{x}$ of corresponding effective Ising model with some $\tilde{J}_{eff}(T,h)$. The explicit expression for the $\tilde{J}_{eff}(T,h)$ follows from the natural constraint

$$\tilde{x}(x=1;T,h) = 1,$$

which according to Eq. (B7) gives

$$\tilde{J}_{eff}(T,h) = T \,\mathrm{arctanh}[p(1;T,h)] - h. \tag{B8}$$

For the models described in Sec. II this procedure gives the value of $\tilde{J}_{eff}(T,h)$ according to

$$\frac{\langle \sinh[\beta \tilde{J}(\sigma)x + h] \rangle_\sigma}{\langle \cosh[\beta \tilde{J}(\sigma)x + h] \rangle_\sigma} = \tanh\left(\frac{\tilde{J}_{eff}(T,h)}{T} \tilde{x} + \frac{h}{T} \right). \tag{B9}$$

Note that because of vanishing of $F(T,h)$ at $x=0$ and $h=0$ it is the excess part of the thermodynamic potential.

APPENDIX C: FLUCTUATION-MULTIPOLE INTERACTION BETWEEN ADMIXTURE MOLECULES

For the sake of simplicity we assume that the structure of H-bond network is only violated in the monomolecular layer adjoint to CCl_4. Such an assumption is verified by the results of computer experiments for ions in water [44]. Due to this, the spontaneous dipole moment $\mathbf{d}^{(s)}$ of the complex-admixture molecule and its nearest surroundings arises [48]. Such an elementary complex may be polarized by the electric field of other elementary complexes and acquires the induced dipole moment $\mathbf{d}^{(i)}$. As a result the interaction energy $U(r)$ of two elementary complexes can be represented in a form

$$U(r) = U_w(r) + U_d(r),$$

where U_w is the potential of standard van der Waals interaction [39] and U_d is the average value of the energy of dipole-dipole interactions:

$$U_d(r)=\langle U(r|\mathbf{d}_1,\mathbf{d}_2)\rangle.$$

The general expression for $U(r|\mathbf{d}_1,\mathbf{d}_2)$:

$$U(r|\mathbf{d}_1,\mathbf{d}_2)=\frac{1}{\epsilon r^3}\left[\mathbf{d}_1\cdot\mathbf{d}_2-3\frac{(\mathbf{d}_1\cdot\mathbf{r})(\mathbf{d}_2\cdot\mathbf{r})}{r^2}\right],$$

where ϵ is the dielectric permittivity of the medium. In accordance with the above,

$$U(r|\mathbf{d}_1,\mathbf{d}_2)=U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)})+U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(i)})+U(r|\mathbf{d}_1^{(i)},\mathbf{d}_2^{(i)}),\qquad\text{(C1)}$$

caused by the spontaneous or induced constituents of dipole moments of two elementary complexes.

To find $\langle U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)})\rangle$ the distribution function $g(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)})$ of spontaneous dipole moments can be approximated by the expression

$$g(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)})=1-\beta U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)}),$$

where $\beta=1/k_BT$, k_B is the Boltzmann constant. It is not difficult to see that

$$\langle U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(s)})\rangle=-\frac{2}{3}\frac{\beta\langle\mathbf{d}_1^{(s)^2}\rangle^2}{\epsilon^2r^6}.\qquad\text{(C2)}$$

In fact this contribution to U_d has the same character and origin as U_w. The difference between them is only connected with the separation of fluctuations of electromagnetic field on intramolecular and extramolecular ones, which characteristic times differ from each other by a factor 10^3.

To calculate the induced dipole moment $\mathbf{d}^{(i)}$ of an elementary complex we will model it by a cavity with the effective dielectric permittivity $\epsilon_c\ll\epsilon$. In the constant electric field such a cavity acquires the dipole moment

$$\mathbf{d}=-\epsilon\frac{1-\tilde{\epsilon}_c}{2+\tilde{\epsilon}_c}r_a^3\mathbf{E}_0,$$

where $\tilde{\epsilon}_c=\epsilon_c/\epsilon$ and r_a is the radius of a cavity. Substituting instead of $\mathbf{E}_0$ the electric field created by the spontaneous dipole moment of another molecule, we obtain

$$\mathbf{d}_2^{(i)}=\frac{1-\tilde{\epsilon}_c}{2+\tilde{\epsilon}_c}\left(\frac{r_a}{r}\right)^3\left[\mathbf{d}_2^{(s)}-3\frac{(\mathbf{d}_2^{(s)}\cdot\mathbf{r})}{r^2}\mathbf{r}\right].$$

Restricting our analysis only by effects caused by the reciprocal influence of two molecules only, we get

$$\langle U(r|\mathbf{d}_1^{(s)},\mathbf{d}_2^{(i)})\rangle=\langle U(r|\mathbf{d}_1^{(i)},\mathbf{d}_2^{(s)})\rangle=\frac{2}{\epsilon}\frac{1-\tilde{\epsilon}_c}{2+\tilde{\epsilon}_c}\frac{\langle\mathbf{d}^{(s)^2}\rangle}{r^6}.\qquad\text{(C3)}$$

The contribution $\langle U(r|\mathbf{d}_1^{(i)},\mathbf{d}_2^{(i)})\rangle$ decays as r^{-9} and can be omitted. Since $\tilde{\epsilon}<(\ll)1$, the interaction of spontaneous and induced dipole moments has the repulsive character. Besides, the contributions (C2) and (C3) depend on ϵ and r_a in different ways. At $r\simeq r_*$, where

$$r_*=\left(\frac{\langle\mathbf{d}^{(\mathbf{s})^2}\rangle}{6\epsilon k_BT}\right)^{1/3},\qquad\text{(C4)}$$

these contributions are reciprocally compensated. To get the numerical estimate for r_* we write

$$\langle\mathbf{d}^{(s)^2}\rangle=d_w^2\xi^2,\qquad\text{(C5)}$$

where d_w is the dipole moment of a water molecule. By order of magnitude the dimensionless parameter ξ satisfies the inequality

$$\zeta\leqslant\xi^2<\zeta^2.\qquad\text{(C6)}$$

The lower limit in Eq. (47) corresponds to the case of uncorrelated dipole moments of these molecules, the upper one corresponds to strong correlations between the dipole moments. From the geometrical reasoning it follows that

$$\zeta\simeq\left(\frac{r_a}{r_s}\right)^2,$$

where r_s is the average size of the solvent molecule. If a solvent is pure water and the admixture molecule is CCl_4: $r_s\sim1$ Å, $r_a\sim4-5$ Å, so $\zeta\sim20$. In this case, as follows from Eq. (C4) and Eq. (C5),

$$r_*\sim0.5\times10^{-8}\zeta^{2/3}\ \text{cm}\sim(2-3)\times10^{-8}\ \text{cm}.$$

A similar estimate is also appropriate for other cases. Hence for admixture molecules with $r_a>r_*$ the repulsive pair interaction by spontaneous and induced dipole moments is dominant. In this case

$$U(r)=U_w(r)+\frac{2\zeta^2}{\epsilon}\frac{1-\tilde{\epsilon}_c}{2+\tilde{\epsilon}_c}\frac{d_w^2}{r_a^3}\left(\frac{r_a}{r}\right)^6.$$

The detailed analysis shows that up to $R_*\sim15-20$ Å the van der Waals contribution to $U(r)$ is small in comparison with the dipole-dipole one (see Ref. [48]). Therefore we expect that all essential peculiarities in the behavior of a solvent at the addition of impurities of type CCl_4 are caused by the potential

$$U(r)\simeq U_d\simeq\frac{2\xi^2}{\epsilon}\frac{1-\tilde{\epsilon}_c}{2+\tilde{\epsilon}_c}\frac{d_w^2}{r_a^3}\left(\frac{r_a}{r}\right)^6.$$

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