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Phase diagram of symmetric binary fluid mixtures: First-order or second-order demixing

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Binary fluid mixtures of 1:1 concentration can demix in a phase transition of first order or of second order. We analyze the two scenarios in density-concentration space and relate them to the structure of the line at which the demixing coexistence surface cuts the liquid-vapor coexistence surface. These scenarios help us to decide between first and second order for a model of a symmetric Lennard-Jones mixture. An optimized reference hypernetted chain integral equation method is employed for calculating the correlation functions and from there the pressure and chemical potentials. We conclude that demixing of a 1:1 mixture is of first order in the whole range of parameters that we have investigated. We did not find a critical point in the 1:1 concentration plane.

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I. INTRODUCTION

In multicomponent systems such as fluid mixtures or in fluids with internal degrees of freedom such as ferroelectric or ferromagnetic liquids or liquid crystals, different types of phase transitions can occur in neighboring regions of the space of thermodynamic variables. For a binary liquid, the liquid-vapor and the mixing-demixing transition can be expected. It is of interest how these phase transitions influence each other, how the regions of different phases meet.

In a series of recent papers by Wilding and co-workers [1–4] especially the case of a second-order demixing transition line confluent with the first-order liquid-vapor transition was studied. A critical end point (CEP) is expected in this situation when the second order demixing line meets the liquid side of the vapor-liquid coexistence line. For higher ''demixing tendency'' the demixing line can meet the critical point of the condensation curve forming a tricritical point [5]. These points are expected to show singularities that were first predicted by Fisher and co-workers [6–8] who also derived universal amplitude ratios and later confirmed the properties of these singularities by model calculations on spherical models [9–11] and on a model ferroelectric [12,13]. The starting point for these considerations is always the supposition that the demixing transition (or the ordering in the case of the ferroelectic) is of second order.

Is the demixing transition of second order? This question we address in this paper. Wilding has studied a model for a symmetrical binary fluid mixture by simulations and has found no contradiction with the assumption of second-order demixing. Also mean field calculations indicate second-order transitions, expecially at elevated temperatures [4,14–22]. The mean field results have lead to a ''generic scenario'' as depicted, e.g., in Fig. 1 of Ref. [4].

The mean field approximation starts from an approximation of the free energy of the system. We have developed approximations, which go beyond ''mean field'' by including calculated correlation functions in the derivation of the free energy. The general density functional approach leads to a hierarchy of equations involving higher-order direct correlation functions [23,24]. The ''mean field approximation'' closes this hierarchy already at the first equation by neglecting correlations altogether or guessing a Boltzmann factor [15–17]. The second level of this hierarchy yields equations for the two particle correlation functions. Closing the hierarchy on this level leads to the integral equations of liquid theory, to hypernetted chain (HNC) [25], reference HNC (RHNC) [26,27], local or weighted density approximations [24,28–34] as well as to the Percus-Yevick equation or mean spherical approximation [25]. After calculating the correlation functions by one of these approximate second level equations one can employ them in the calculation of the free energy at the first level of the hierarchy. Under several circumstances we have shown, that a careful calculation of the correlation functions can lead to reliable free energies [33–38]. This is shown again in Fig. 5 for the case of a binary mixture with Lennard-Jones interactions.

When studying a dipolar hard sphere liquid we have met already a case where mean field calculations had predicted a λ line of critical points for the transition to the dipolar order [15], while our free energy with calculated correlations saw the transition as first order with a jump in density and order parameter [36]. We, therefore, apply similar methods here to analyze the demixing transition in a model binary fluid mixture. The model is the same as the one used in the simulations by Wilding, a symmetric mixture with equal A-A and B-B Lennard-Jones interactions and decreased A-B interaction.

In numerical calculations, simulations as well as our integral equation solutions, it is generally difficult to get results at all close to critical points and to distinguish between second-order and weak first order. We show in Sec. IV how such a decision can be obtained.

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After fully defining the model (see Sec. II), the paper discusses first some general properties of the phase diagram of such a symmetric binary mixture (Sec. III). We learn where to look for coexisting phases and then in Sec. IV we find a method to decide that in all the cases that we have investigated, the demixing transition is of first order. Some discussion and conclusions are summarized in Sec. V.

II. THE BINARY LIQUID MIXTURE MODEL

We will study a mixture of two fluid species *A* and *B*. The particles interact via Lennard-Jones potentials

$$U_{ij}(r)=4\varepsilon_{ij}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1}$$

As in the previous investigations [2,4,14,39,40] we reduce the space of variables by taking the same diameters σ for all interactions and setting $\varepsilon_{AA}=\varepsilon_{BB}$ for the mutual interaction between particles of the same kind. This equality leads to a symmetry of the free energy of the system with respect to the exchange of the densities ρ_A and ρ_B. The binding of the particles of different kind, ε_{AB}, is taken smaller, i.e., $\alpha=\varepsilon_{AB}/\varepsilon_{AA}<1$. This fact induces a demixing phase transition at lower temperatures and higher densities, when the potential energy can be lowered by demixing, which avoids the weak *A*-*B* bonds. We can increase the tendency for demixing in the model by lowering α. Then demixing will already occur at higher temperatures and lower densities.

III. THE PHASE DIAGRAM OF THE SYMMETRIC BINARY FLUID MIXTURE

A. Consequences of symmetry

We want to discuss the phase diagram in the plane of the variables total density $\rho=\rho_A+\rho_B$ and concentration $c=\rho_A/\rho$. When we imagine as the third dimension the temperature T ($T^*=k_BT/\epsilon_{AA}$) we can draw the surfaces of coexistence points, see Fig. 1. When the tendency for demixing is small, i.e., $\varepsilon_{AB}/\varepsilon_{AA}=\alpha$ close to (but smaller than) 1, we get at low densities a liquid-vapor surface with a line of critical points along the concentration direction. At higher densities, where in the free energy the potential energy dominates over the entropy, we get a demixing surface with a leading edge at equal concentration $c=0.5$, because here the lowering of potential energy on demixing is largest. The smallest density for demixing (at fixed T) is found in a 1:1 mixture.

The coexistence surfaces are symmetric with respect to the plane $c=0.5$, because the free energy of our system stays unchanged, if we go from concentration c to $1-c$ for fixed density ρ; only the ratio of minority molecules to majority matters irrespective of *A* or *B*. For clarity Fig. 1 leaves out the very low temperatures. At lower temperatures the two surfaces cut each other. We imagine that by lowering α we move the demixing surface to lower densities (and higher T) and this way make the surfaces cut. From drawing the surfaces of coexistence points it is not yet clear which phases really coexist: If a vapor of concentration c_1 is compressed the coexisting liquid might have a different concentration c_2. What does the symmetry of the diagram, of the free energy or of the interraction allow us to conclude about the demixing coexistence surface?

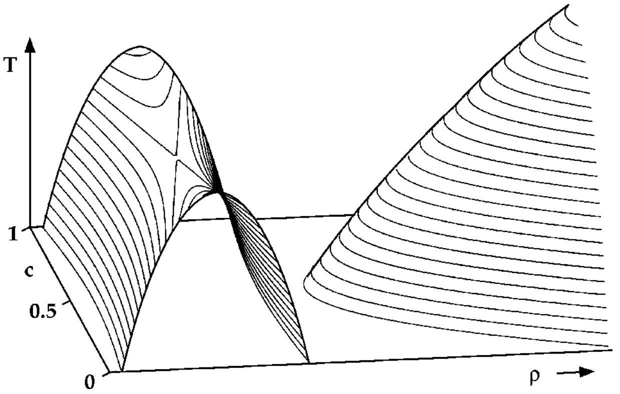

FIG. 1. Schematic view of the coexistence surfaces: For gas-liquid coexistence at the left, for demixing at the right.

Let us consider the case where two coexisting demixing phases lie symmetric with respect to concentration (at common ρ and at c and $1-c$). Symmetry requires

$$\mu_A(c)=\mu_B(1-c), \tag{2}$$

$$\mu_B(c)=\mu_A(1-c).$$

Coexistence at symmetric points says

$$\mu_A(c)=\mu_A(1-c)\Rightarrow\mu_A(c)=\mu_B(c).$$

The conclusion is that only phases, with $\mu_A=\mu_B$ within the same phase at c can coexist with the symmetric phase at $1-c$. Obviously a fluid with $\mu_A=\mu_B$ at (ρ,c) has in any case a coexisting partner at $(\rho,1-c)$. We, therefore, expect that part of the coexistence surface for demixing is determined by $\mu_A=\mu_B$ within the same phase. The coexisting phases then have the same density ρ and concentrations c and $1-c$.

On the plane $c=0.5$ that was studied by Wilding and coworkers [1–4] $\mu_A=\mu_B$ because of symmetry. In Fig. 2 we show a cut at fixed temperature T through the surfaces of Fig. 1. We will imagine compression of the fluid along the symmetry line $c=0.5$. At point II in Fig. 2 the surface $\mu_A=\mu_B$ meets the symmetry plane. If demixing occurs at this point it will be of second order: The difference in concentration grows continuously from zero and the coexisting phases move along the $\mu_A=\mu_B$ surface for increasing density or pressure. A surface $\mu_A=\mu_B$ (line $\mathrm{I_b}$-II-$\mathrm{I_a}$ in Fig. 2) can be expected due to the changes of the order of μ_A and μ_B as indicated in Fig. 2. For low densities $\mu_{minority}<\mu_{majority}$ because of the entropy of mixing; for high densities it is more favorable to add a majority particle with strong binding potential than a minority particle with weak *A*-*B* interactions, therefore, $\mu_{minority}>\mu_{majority}$.

Another scenario is possible where at I (Fig. 2) demixing occurs and phases $\mathrm{I_a}$ and $\mathrm{I_b}$ necessarily on the line $\mu_A=\mu_B$, are formed in a first order transition and coexist with I. From I starts a line of first-order coexistence points con-

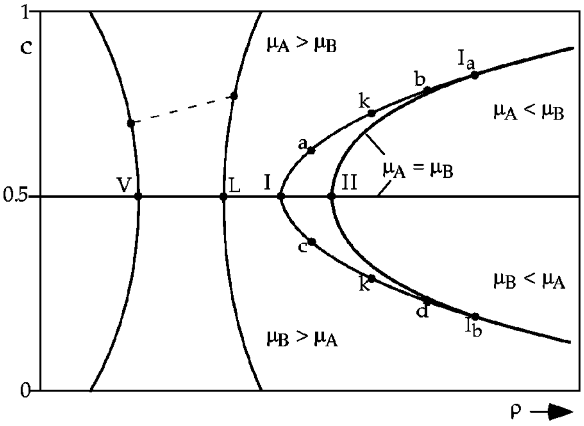

FIG. 2. Schematic cut at constant T through the coexistence surfaces.

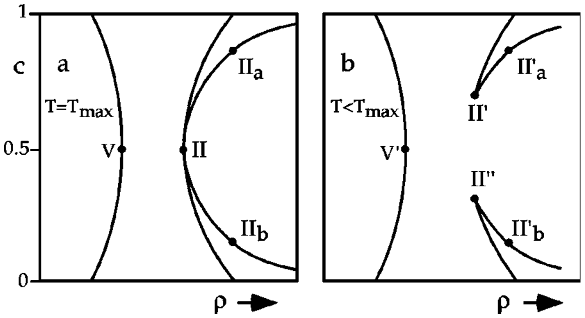

FIG. 3. Same as Fig. 2 for the type of contact of the two surfaces that leads to second-order demixing.

necting to $\mathrm{I_a}$ and $\mathrm{I_b}$. Here the points a and b coexist as well as c and d, but not a and c. This conclusion derives from the fact, that the curves $\mu_A(c,\rho)$ and $\mu_B(c,\rho)$ considered along the line I-a-b-$\mathrm{I_a}$ cross at I and at $\mathrm{I_a}$. On the first-order line between a and b there will be a critical point k where the μ_A and μ_B curves along the coexistence line simultaneously have their extrema.

So the demixing surface will be partly a surface $\mu_A(c) = \mu_B(c)$ with symmetric coexisting phases c and $(1-c)$. A part of it towards smaller densities can be a surface of first-order transitions with both coexisting phases on the same side of $c=0.5$ and two λ lines of critical points symmetric at concentrations away from $c=0.5$. The two symmetric phases that coexist with the mixed phase at $c=0.5$ ($\mathrm{I_a}$ and $\mathrm{I_b}$ in Fig. 2) border that part of the coexistence surface where coexisting phases are symmetric at c and $1-c$ with $\mu_A(c) = \mu_B(c)$.

If the temperature of the cut (Fig. 2) increases the two critical points k on the first-order surface will move closer together as will the points $\mathrm{I_a}$ and $\mathrm{I_b}$ because the larger weight of the entropy in the free energy favors mixing, smaller concentration differences. It might happen that finally the points I,k,I_a,$\mathrm{I_b}$ all converge to point II which then becomes the low temperature end, a tricritical point, of a λ line of critical points at $c=0.5$.

We can ask whether there can be coexistence between points not on the surface $\mu_A = \mu_B$ for densities higher than those of $\mathrm{I_a}$ and $\mathrm{I_b}$ in Fig. 2 We could not think of a scenario where this situation did not lead to a violation of Gibbs' phase rule when the symmetry and the continuous connections where considered.

B. Topology of the cut of the coexsistence surfaces and the order of the demixing transition

We now want to understand how the topology of the cut between the liquid-vapor surface and the demixing surface is related to the order of the demixing transition. We consider the line in (ρ,c,T) space, at which the two surfaces cut and show:

If this cut line at the symmetry point $c=0.5$ has a maximum with respect to T, then this symmetry point is a CEP and the demixing is of second-order for higher T. If the cut has a local minimum at $c=0.5$ the demixing transitions in the neighborhood are of first-order.

The first case (maximum) is shown in Figure 3 with two slices at two temperatures T_{max} and $T<T_{max}$: Fig. 3(a) has T_{max} exactly equal to the maximum temperature of the cut, at which the liquid line and the demixing line have only this maximum point II in common. Here V and II coexist because $\mu_A = \mu_B$ at $c=0.5$. If demixing would be of first order II would also coexist with phases $\mathrm{II_a}$ and $\mathrm{II_b}$ a discrete distance away from II into which the system would demix when the density is further increased after the vapor at V has been completely compressed into the liquid at II. At a temperature infinitesimally smaller than T_{max} [the cut Fig. 3(b)], V' coexists either with II$'$ and II$''$, the neighbors of II, or with II_a' and II_b', the neighbors of $\mathrm{II_a}$ and $\mathrm{II_b}$, respectively, because μ changes continuously with T. The first case, V' with II$'$ and II$''$, leads to the fact that on the line II$'$ to II_a' and II$''$ to II_b' is $\mu_A = \mu_B$ and at T_{max} the whole demixing line is of type $\mu_A = \mu_B$. Therefore demixing is of second order at II under further compression that contradicts the coexistence of II with $\mathrm{II_a}$ and $\mathrm{II_b}$. If in the second case V' coexists with II_a' and II_b' and not with II$'$ and II$''$, II$'$ must coexist with one point on the vapor line (say $\tilde{V}$) a discrete distance from V'. Points between $\tilde{V}$ and V' coexist with points between II$'$ and II_a' for reasons of continuity. On approaching $T=T_{max}$ II$'$ goes to II, $\tilde{V}$ to V and II_a' to $\mathrm{II_a}$. We conclude that now the whole interval between II and $\mathrm{II_a}$ must coexist with V, an impossible situation. Therefore first-order demixing at II in Fig. 3 is ruled out. Demixing at II is of second order; i.e., the difference in concentration of the coexisting phases goes to zero here if the point II is approached from higher densities or from lower temperatures. II is then a CEP of a λ−line coming down from higher T at $c=0.5$.

In the case where the cut line has a minimum at $c=0.5$ we show that this minimum point must be a point of first-order demixing transition. Figure 4 depicts the structure of two temperature slices: for T_1 just above T_{min} (at which the line L,b,I,c would shrink to a point) and at $T_2>T_1$ above which the liquid surface and the demixing surface do not touch anymore. The essential difference to the case of Fig. 3 is the fact, that in the neighborhood of the point where the two surfaces touch at $c=0.5$ [point of convergence of L and I in Fig. 4(a)] there are *two* disconnected forbidden regions (of

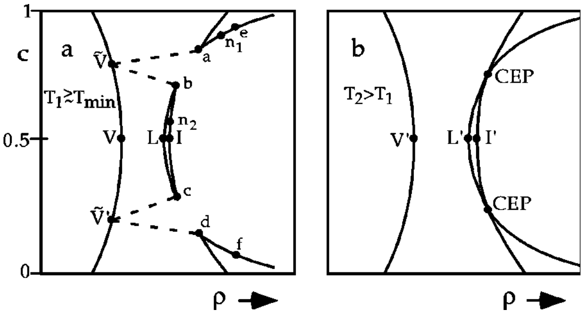

FIG. 4. Same as Fig. 2 for the type that is connected with first-order demixing.

metastability or instability, between a and b and between c and d). On the slice just below T_{min} the vapor at $c=0.5$ coexists with the neighbors of a and d. Above T_{min} V coexists with L [Fig. 4(a)]. Further compression will lead to demixing at I. If this demixing would be of second order, we would have coexisting phases at c and $1-c$ symmetrical to I. Due to this symmetry also b and c would coexist. But if one compresses the vapor at $c \neq 0.5$ one can conclude, that there must be a point $\tilde{V}$ on the vapor line in Fig. 4(a), which coexists simultaneously with a and b. Also the symmetric phases c, d, and $\tilde{V}'$ coexist. If now b and c would coexist we would have six, too many, coexisting phases. The only way out which we see is a first-order nonsymmetric decomposition in the neighborhood of I. I will coexist with e and f and demix in first-order. Then it is possible that the neighbor n_1 of e moves to point a and coexists with the neighbor n_2 of I moving to b until finally a, b, and $\tilde{V}$ coexist. Gibbs' phase rule that states

$$(\text{thermodynamic degrees of freedom})$$

$$=(\text{number of components})+2-(\text{phases})$$

can be saved because $\tilde{V},a,b$ do not coexist with the symmetric system $\tilde{V}'$, c, d. The points a,b,c,d must be in regions of the coexistence surface where $\mu_A(c) \neq \mu_B(c)$ (see Fig. 2), therefore, a symmetrical second-order demixing transition starting at I is not possible.

At higher temperatures [Fig. 4(b)] we expect a and b moving together into a critical point with a symmetrical counterpart at c,d [CEP in Fig. 4(b)]. These critical points are the end points of the two λ lines of critical points on the demixing surface (at $c \neq 0.5$) that were discussed before and that cross the constant T cut of Fig. 2 in k.

We last discuss which situation, minimum or maximum, has to be expected. This depends on the curvature of the two surfaces when they meet. In our system, where demixing is introduced by reduction of the binding between the molecules of different kind, the liquid curve at a given temperature is convex towards lower densities, because at $c=0.5$ the cohesion and, therefore, the liquid density coexisting with the vapor is decreased compared to the pure A or B liquids. The same reason leads to a decreased critical temperature for the vapor-liquid transition at $c=0.5$. Also the demixing curve has the same convexity, because the smallest density for the demixing is always found at $c=0.5$, where the gain in potential energy on demixing is largest. For c towards 1 or 0 the demixing needs very low temperatures or very high densities, so the cutting line between the two surfaces goes to low temperatures in these regions. If at fixed temperature the convex curvature of the demixing surface near $c=0.5$ is larger than that of the liquid phase surface, the surfaces will touch at one highest temperature T_{max} and the touching point will be a critical end point according to the arguments around Fig. 3 [point II in Fig. 3(a)]. When the demixing surface is less curved than the liquid side of the vapor-liquid surface, the first touch between the surfaces, when one moves down from higher temperatures, will be at two symmetrical points [CEP in Fig. 4(b)] and lower temperatures are necessary to hit the touching point at $c=0.5$, which is then a local minimum of the cut line between the vapor liquid and the demixing surface with the consequence of first-order demixing and two CEP's symmetrically at $c \neq 0.5$, as explained in connection with Fig. 4.

If the potential parameters of the model are such, that the cut of the two surfaces at $c=0.5$ is close to the critical vapor-liquid point, we always expect the first-order scenario (Fig. 4). The critical point of the condensation at $c=0.5$ is a saddle point and, in general, constant temperature lines on the vapor-liquid coexistence surface will cut, i.e., will have infinite curvature at this point. Therefore in this neighborhood the demixing surface will first touch at two regions $c \neq 0.5$ before it touches at the symmetry point $c=0.5$, considering it from higher temperatures downwards. This last conclusion indicates only a good chance for first-order demixing, but when the demixing surface meets the liquid-vapor surface near the critical point for condensation, the two surfaces influence each other and may deform.

This concludes the general discussion of the phase diagram scenarios for a symmetric binary fluid mixture. When tuning the demixing strength α in our model we can generally expect a region of first-order demixing. We will ask in the following section, if we at all find a symmetrical Lennard-Jones mixture where demixing of a fluid with $c=0.5$ is a transition of second-order.

IV. RESULTS OF MODEL CALCULATIONS

We now apply model calculations to investigate which of the possible scenarios we find for the case of a symmetrical Lennard-Jones mixture. We use a RHNC calculation [26,27] for deriving the correlation functions and employ those for the calculation of the thermodynamic properties: the chemical potential and the pressure at chosen temperature, density, and concentration. We have optimized the calculation by choosing the diameter of the reference hard sphere system such that the calculated free energy A, chemical potentials μ_α and pressure P are as consistent as possible by minimizing [41]

$$\Delta^{\mathrm{RHNC}}=A/V-\left(\sum_{\alpha} \mu_\alpha \rho_\alpha - P\right). \tag{3}$$

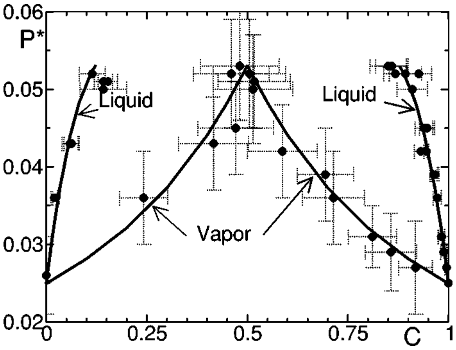

FIG. 5. Liquid-vapor coexistence curves for a binary mixture. The coexisting concentrations are shown at given pressure $P^* = P\sigma^3/\epsilon_{AA}$, $\epsilon_{AB}/\epsilon_{AA} = 0.7, T^* = 1$. Dots are simulation results from Ref. [39].

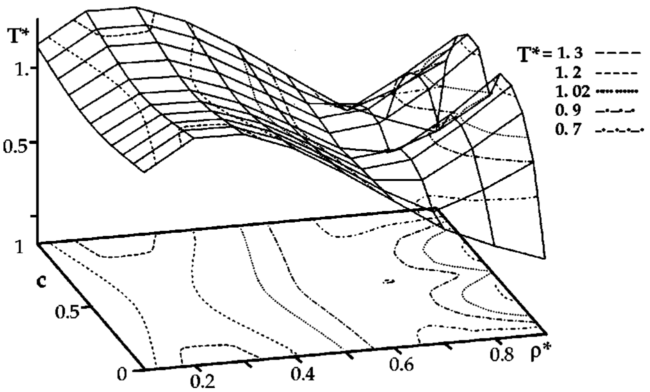

FIG. 6. The "spinodal" surface for a mixture with $\epsilon_{AB}/\epsilon_{AA} = 0.81$.

This quantity could actually be made zero in all cases investigated and we have shown in other circumstances, that the thermodynamic properties derived this way are extremely accurate when compared to simulation results [34]. We demonstrate this in Fig. 5 by comparing our coexistence curves at a fixed temperature $T^* = kT/\varepsilon_{AA} = 1$ to GEMC simulation results for a symmetrical Lennard-Jones mixture with $\alpha = \varepsilon_{AB}/\varepsilon_{AA} = 0.7$ by Lopes [39,40]. In our calculation we find the points on the coexistence curve by searching for two phases $(\rho^{\mathrm{I}}, c^{\mathrm{I}})$ and $(\rho^{\mathrm{II}}, c^{\mathrm{II}})$ with $\mu_A^{\mathrm{I}} = \mu_A^{\mathrm{II}}$, $\mu_B^{\mathrm{I}} = \mu_B^{\mathrm{II}}$ and pressure $P^{\mathrm{I}} = P^{\mathrm{II}}$. The agreement with the simulation results is very satisfactory and proves the reliability of our free energy and thermodynamic data.

The temperature in Fig. 5 is rather low and, therefore, the vapor-liquid phase transition as well as the demixing is not close to possible critical regions. When these regions are approached, experiments and model calculations get into problems. With our method the problem is the appearance of regions in phase space where the integral equation have no solutions, where integrals over correlation functions get infinite, because fluctuations and corresponding susceptibilities get infinite [25,42]. Due to the approximations these instability regions (which should correspond to regions below the spinodals or beyound critical regions) cover near critical points the coexistence region and make it inaccessible for this method of calculation [38]. In addition to parts of the coexistence surface our calculation, therefore, yields a surface of an inaccessible region, a "spinodal" surface.

For the case of $\alpha = 0.81$ this surface is shown in Fig. 6 [43]. We see two symmetrical hills with a deep valley near $c = 0.5$. It means that we have to expect critical regions symmetrical at $c \neq 0.5$, but on the plane $c = 0.5$ fluctuations or compressibilities do not appear to be large and, therefore, it is improbable that we have there second-order transitions.

We have discussed in Sec. III A that for $c = 0.5$ a second-order transition can only happen at the point, where the line $\mu_A(\rho, c) = \mu_B(\rho, c)$ crosses the symmetry line $c = 0.5$ (in a cut at fixed temperature) (point II in Fig. 2). We, therefore, investigate this neighborhood by calculating μ and P. Figure 7 shows a graph of results for such a case. We find a rising line of $\mu_{A,B}(c = 0.5)$ with increasing ρ and P. When the line $\mu_A = \mu_B$ at $c \neq 0.5$ crosses the line for $c = 0.5$ (at point II in Fig. 2), we find $\mu_{A,B}$ rising on this line above $\mu_{A,B}(c = 0.5)$. This fact rules out the demixing phase transition because the Gibbs free energy would grow when demixing would set in, instead of going into the minimum. The system, therefore, would stay mixed. In our opinion this calculation shows that there is no second-order transition on the line $c = 0.5$ for $\alpha = 0.8$ and $T^* = 1$. Then only a first-order transition is possible. The coexisting phases in this case must also lie on the line $\mu_A = \mu_B$ (see points $\mathrm{I_a}, \mathrm{I_b}$ in Fig. 2). We see, that the (μ, P) points in Fig. 7 form a typical first-order instability loop. We cannot follow the whole loop because we encounter the instability region of our calculation, but at larger distance from the $c = 0.5$ line we can evaluate $\mu_A = \mu_B$ again and find it well below the values at $c = 0.5$. We, therefore, conclude, that the dash-dotted (μ, P) curve of Fig. 7 turns back and cuts the (μ, P) line for $c = 0.5$ at a point different from the cross point in Fig. 7. The point of this cut is the first-order transition point shown as point I in Fig. 2. The parameters ρ and c for the cut yield the coexisting phases I, $\mathrm{I_a}$, $\mathrm{I_b}$ in Fig. 2.

We believe that by finding μ above $\mu_{A,B}(c = 0.5)$ near the crossing point of the $\mu_A = \mu_B$ lines we can decide that the demixing phase transition is of first order. We have carried out this investigation in the region $0.25 < \alpha < 0.81$ and al-

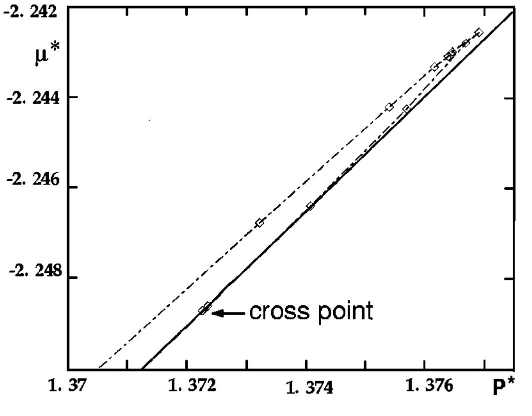

FIG. 7. The chemical potential $\mu^* = \mu/\epsilon_{AA}$ on the line $c = 0.5$ (——) and on the line $\mu_A = \mu_B$ $(- \cdot - \cdot -)$ for $\epsilon_{AB}/\epsilon_{AA} = 0.8$, $T^* = 1$, $P^* = P\sigma^3/\epsilon_{AA}$.

ways found first-order. Especially also in the region $\alpha = 0.7$ and $T^* \approx 1$, where Wildings simulations [2] indicate a second-order transition, our calculations say first order. Because of the instability region in our procedure, we cannot derive the density of the phases that coexist with the one at $c = 0.5$. It could be that the jump in the density and in concentration is so small that a simulation has difficulty distinguishing it from a continuous second-order transition.

V. CONCLUSIONS

We have discussed the order of the demixing phase transition of a symmetrical binary fluid mixture.The symmetry of the molecular interactions makes the free energy and all thermodynamic quantities symmetric with respect to exchange of the particles of kind A and B. This symmetry together with considerations of continuity of phases with continuous change of parameters and Gibbs phase rule made it possible to get complete information about the scenarios of first-order and of second-order demixing. It was possible to connect these scenarios to the way the demixing coexistence surface and the liquid-vapor coexistence surface cut each other:

When the cut line of these two surfaces crosses the symmetry plane $c = 0.5$ in a *maximum* with respect to T, at T_{max}, the demixing at $T > T_{max}$ for $c = 0.5$ is of *second order*. The line $c = 0.5$ on the demixing surface is a line of critical points with a CEP at T_{max}.

When the cut line has a *local minimum* at $c = 0.5$ with respect to T the demixing in the neighborhood of this point is of *first-order*. There exist two critical lines symmetrically away from $c = 0.5$ with two CEP's at two symmetrical maxima of the cut line at $c \neq 0.5$. At higher temperatures these critical lines can meet at $c = 0.5$ and from thereon to higher T demixing at $c = 0.5$ would be of second-order. We have argued that the first-order scenario is very probable when the two surfaces meet near the critical point of the liquid-vapor transition at $c = 0.5$.

Finally we have made model calculations for a Lennard-Jones mixture with equal A-A and B-B interactions and decreased A-B interactions. With the optimized RHNC integral equation method we calculated the correlation functions and determined pressure and μ_A, μ_B for given T, ρ and c. Testing then the second-order scenario shows that the Gibbs free energy of the demixed phases lies above that of the mixed phase. Therefore the other alternative applies: *Demixing is of first order*. We think that our method can distinguish between second order and weak first order, which is difficult also for simulations or even experimentally.

We have searched over a wide range of parameters of our model $(0.25 \leqslant \epsilon_{AB}/\epsilon_{AA} \leqslant 0.81)$ and *did not find a case of second-order demixing* on the symmetry plane $c = 0.5$ for the symmetric Lennard-Jones mixture.

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