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Type-IV phase behavior in fluids with an internal degree of freedom

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We have identified a fourth archetype of phase diagram in binary symmetrical mixtures, which is encountered when the ratio of the interaction between the unlike and the like particles is sufficiently small. This type of phase diagram is characterized by the fact that the λ line (i.e., the line of the second-order demixing transition) intersects the first-order liquid-vapor curve at densities smaller than the liquid-vapor critical density. © *2005 American Institute of Physics*.
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The first systematic investigations on the phase behavior of binary symmetrical fluid mixtures have been presented in Ref. 1. In such a system the interaction between particles of the same species (labeled "1" and "2") is equal, i.e., $\Phi_{11}(r)=\Phi_{22}(r)$, while the potential between unlike particles is fixed via $\Phi_{12}(r)=\alpha\Phi_{11}(r)$. Often it is convenient to view such a binary mixture as a one-component fluid whose particles carry an internal degree of freedom.[1] We point out that as a consequence differences to other conventions might occur, where, for instance, the demixed phase is counted as two independent phases.[2] For $\alpha<1$ we expect three phases: the homogeneous vapor, the homogeneous fluid, which is also called mixed fluid (MF), and the two symmetrical demixed phases (DFs), which are counted as one single phase and the internal degree of freedom indicates whether this phase is 1 or 2 rich. The interesting phase phenomena encountered for this system result from an interplay of two competing transitions, i.e., the line of the second-order demixing transition (critical line at $x=0.5$, termed in the literature often as λ line) and the first-order liquid-vapor (LV) transition. Already in the field-free case, i.e., when the difference in the chemical potentials of the two species is zero, we observe a rather complex phase behavior: three archetypes of the phase diagrams have been identified up to now, depending on how the λ line intersects the first-order LV coexistence line. Using a typology that had been introduced in a related context (see also below),[3] the three cases are characterized as follows (see Fig. 1 of Ref. 1): (i) In the type-I phase diagram the λ line approaches the LV coexistence boundary at temperatures well below its critical temperature T_{cr} intersecting this curve in a critical end point (CEP). Above the CEP temperature T_{CEP}, the vapor and the mixed liquid of intermediate density coexist; they become identical at the LV critical point. The fluid demixes at higher densities as one crosses the λ line. The coexistence line below the CEP is a two-phase line where the vapor and the demixed phase coexist. (ii) In the type-III phase diagram, the λ line intersects the LV coexistence line at the LV critical point, resulting in a tricritical point where the vapor and the demixed phase become critical simultaneously. The first-order transition between the vapor and the mixed liquid is completely suppressed. (iii) In the type-II phase diagram the intermediate situation is realized: the λ line approaches the LV coexistence curve slightly below the LV critical temperature. As in type I one finds a LV critical point and, similar as in type III, a tricritical point is observed. In addition, a triple point is encountered where the vapor, the mixed liquid at intermediate density, and the demixed phase at higher densities coexist.

Obviously α represents an external parameter that is responsible for the transition from one topology of phase diagram to the next. Confirmed by subsequent investigations of other binary symmetrical mixtures[4–9] and using liquid-state theories of different levels of sophistication the following scenario is by now well established: even though the specific α value where one type of phase diagram transforms in the subsequent one will distinctively depend on the particular potential and the liquid-state theory applied, the sequence of types remains unchanged, i.e., I(at large α) $\leftrightarrow$ II $\leftrightarrow$ III(at small α).

In an effort to establish a link to the classification scheme of van Konynenburg and Scott,[10] we have summarized in Table I translation rules between the types of van Konynenburg and Scott and those introduced by Tavares *et*

TABLE I. Correspondence between the types of binary symmetric mixtures classified by van Konynenburg and Scott (see Figs. 1 and 38 of Ref. 10) and the types I, II, III, and IV introduced by Tavares *et al.* (Ref. 3). Types II-α and II-β are subtypes of type II that are described in more detail in Ref. 15.

	van Konynenburg and Scott		Tavares
$\Lambda<0$	I-A	$\alpha>1$	no demixing
$\Lambda>0$	II-A	$\alpha<1$	I
	II-A*		II-α
	III-A*		II-β
	III-HA		III
	not classified		IV

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al.[3] In their study of binary van der Waals mixtures van Konynenburg and Scott have introduced three parameters to characterize the mixture: ξ, ζ, and Λ. Our binary symmetric mixture corresponds to $\xi=0$ since particles are of equal size and $\zeta=0$ since the like particle interactions are equal. Their parameter Λ can be related to our parameter α (see below).

Interestingly, these three topologies of phase diagrams were also encountered in other systems: Heisenberg fluids[3,11] and Stockmayer fluids;[12] "translation rules" can be provided that prescribe how the vapor, the mixed, and the demixed phases of the present model "translate" into the coexisting phases of the respective system. Even though these systems obviously describe a completely different scenario, in a wider context they can be considered as one-component fluids with an additional internal degree of freedom (such as the dipolar and magnetic moments, or the particle species label). Thus they form one class of systems and are therefore characterized by the same archetypes of phase diagrams. In each of them a parameter can be identified that takes over the role of α, triggering thus the consecution of types of phase diagrams which in all cases reads I $\leftrightarrow$ II $\leftrightarrow$ III. We conclude by pointing out that the same types of phase diagrams are encountered if above fluids are exposed to external fields, such as classical spin fluids in an external magnetic field[13] or fluids in contact with porous materials.[14] The change between the types of phase diagrams is then triggered by a complex interplay between the internal degree of freedom and the external field.

This nice and consistent scenario is only disturbed by the fact that a fourth type of phase diagram had been encountered in Heisenberg fluids[3,11] but not in the other systems mentioned above: in the literature it is denoted as type IV.[3] Here the λ line intersects the LV coexistence curve at a CEP at a density which is smaller than the density of the LV critical point.

In the present contribution we report about our investigations to localize this type of phase behavior in binary symmetrical mixtures. These efforts are motivated and justified by the fact that for this system—being undoubtedly the simplest representative in this class of systems—systematic investigations can be carried out much easier than in any other case. Simplifications in the conceptual and computational complexity with respect to the other systems of this class become, in particular, apparent when an external field is applied.[15] The liquid-state theories we have used are based on the mean spherical approximation (MSA), i.e., an approach that clearly goes beyond the mean-field level and is thus able to provide also quantitative information about the phase behavior. In particular, for the system of our choice, a binary symmetrical hard-core Yukawa (HCY) mixture, MSA can be solved to a large extent analytically,[16,17] which represents an additional and not negligible advantage over other systems of this class, which, in general, require a significantly larger amount of numerical and conceptual efforts. In addition, we have used the self-consistent Ornstein-Zernike approximation[18] (SCOZA), an advanced liquid-state concept, which is able to provide even quantitative predictions for the phase boundaries and for the location of the critical points.

We have indeed found type-IV phase behavior for our binary symmetrical mixture: it is realized as α is decreased below the α range that characterizes the type-III topology. To reestablish the link to the van Konynenburg and Scott classification scheme we point out that our particular choice of α (i.e., $\alpha=0$) corresponds in Ref. 10 to $\Lambda=1$; as can be seen from Fig. 2 of Ref. 10 this region had not been investigated by these authors. The reasons why this type of phase behavior had not been encountered in the numerous investigations of binary symmetrical mixtures performed up to now remain rather obscure, in particular, in view of the fact that its possible existence was already surmised on a qualitative level in Ref. 1 (and referring further details to Ref. 19). One plausible justification might be related to the fact that we had to face considerable numerical problems to solve MSA and SCOZA for this particular archetype (see below).

Our investigations are based on a binary symmetrical HCY mixture, where particles of species i and j interact via potentials $\Phi_{ij}(r)$, given by

$$\beta\Phi_{ij}(r) = \begin{cases} \infty, & r \leqslant \sigma \\ -\dfrac{K_{ij}}{r}\exp[-z(r-\sigma)], & r > \sigma, \end{cases} \tag{1}$$

with $i,j=1,2$; $\beta=(k_BT)^{-1}$ (k_B being the Boltzmann constant and T the temperature), σ is the hard-core (HC) diameter which will be used as the unit of length, and z is the inverse screening length of the system. Symmetry imposes $K_{11}=K_{22}$ and the parameter α relates the unlike to the like interactions via $K_{12}=\alpha K_{11}$; in this contribution $\alpha<1$. The total number density is $\rho=\rho_1+\rho_2$, where ρ_1 and ρ_2 are the partial number densities and $x=\rho_1/\rho$ is the concentration of species 1 (or also called molar ratio). Reduced values $z^\star=z\sigma$, $\rho^\star=\rho\sigma^3$, and $T^\star=\sigma/K_{11}$ will be used throughout the paper; for simplicity we drop the stars from now onwards. We point out that we only consider the equimolar (or field-free) case.

MSA and SCOZA are based on the same closure relation to the Ornstein-Zernike (OZ) equations which reads for the present model,

$$\begin{aligned} &g_{ij}(r) = 0 \quad \text{for } r \leqslant 1, \\ &c_{ij}(r) = c_{\mathrm{HC};ij}(r) + K(\rho,T,x)\Phi_{ij}(r) \quad \text{for } r > 1. \end{aligned} \tag{2}$$

We have introduced the direct correlation functions $c_{ij}(r)$ and the pair distribution functions $g_{ij}(r)$, $i,j=1,2$, and $c_{\mathrm{HC};ij}(r)$ are the direct correlation functions of the HC reference system. For MSA, $K(\rho,T,x)\equiv-\beta$ while in the SCOZA framework the yet undetermined state-dependent function $K(\rho,T,x)$ is fixed by the global thermodynamic self-consistency requirement for the isothermal compressibility, calculated via the compressibility and the energy route. We point out that—depending on the system parameters—a small degree of inconsistency remains.

The rather complex formalism of SCOZA (for details we refer to Refs. 7, 9, and 20) largely takes benefit of the availability of the analytic MSA solution for a HCY mixture with an arbitrary number of components.[16,17] This justifies *a posteriori* our choice for this particular system, which, as we explicitly point out, does not represent any restriction: any

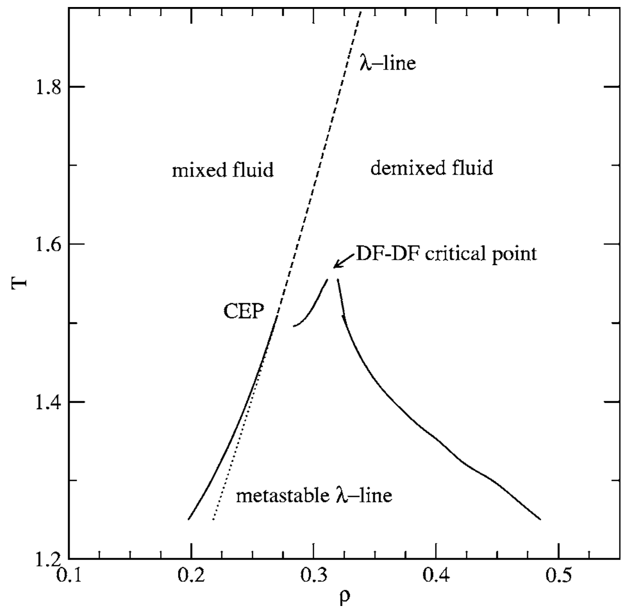

FIG. 1. Type-IV phase diagram of a binary symmetrical HCY mixture with $z=1.8$ and $\alpha=0$ calculated within SCOZA: the full line is the coexistence line, the dashed line is the stable λ line, and the dotted line is the metastable λ line. The full line corresponds to the MF-DF coexistence line below the CEP temperature T_{CEP} and the DF-DF coexistence line above T_{CEP}.

other binary symmetrical mixture with a different (short-ranged) potential would have lead on a *qualitative* level to the same results.

Once MSA or SCOZA have been solved, the thermodynamic properties of the system can readily be calculated. In particular, we require the pressure P and the chemical potentials μ_1 and μ_2 for the determination of the phase diagram. The coexistence equations have been solved with well-tested numerical algorithms, taking benefit of some symmetry relations in μ's due to the symmetry in the interactions (again, for details, see Refs. 7 and 20).

In Fig. 1 we show the phase diagram of a particular HCY system obtained within SCOZA, characterized by $z=1.8$ and $\alpha=0$, corresponding to a pure HC repulsion between particles of different species. The λ line intersects the first-order LV coexistence curve on the low-density (i.e., on the vapor) side in a CEP. Above the LV critical temperature T_{cr} we observe a mixed fluid at lower densities and a demixed fluid at higher densities. In the temperature range below T_{cr} and above T_{CEP} two-phase coexistence between a demixed fluid of intermediate and a demixed fluid of high density is observed, the two phases becoming identical above T_{cr}. If one decreases the temperature to T_{CEP} a critical DF of intermediate densities coexists with a noncritical DF of higher densities; below T_{CEP} one finds coexistence betweeen a homogeneous vapor and a DF at higher densities.

From the numerical point of view, the determination of the type-IV phase diagram is considerably more delicate than in the other three archetypes. First, close to T_{cr} and T_{CEP} the solution algorithms for the coexistence equations break down; we therefore leave the respective regions open. The more serious numerical problems we had to face in the type-IV topology are the following: the surface $\mathcal{S}_{\mathrm{stab}}$, where $(\partial^2 G/\partial x^2)=0$, G being the Gibbs free energy, separates stable from unstable states (e.g., cf. discussion in Ref. 17). In a fully self-consistent approach, this surface touches the coexistence surface for the demixing transition, $\mathcal{S}_{\mathrm{demix}}$, along the λ line and this is, e.g., the case as $z \to 0$: SCOZA (and MSA) become *fully* self-consistent and we have indeed observed[9] that $\mathcal{S}_{\mathrm{stab}}$ and $\mathcal{S}_{\mathrm{demix}}$ touch along the λ line. For larger z values this consistency is violated (to a moderate degree); if α is sufficiently large, then $\mathcal{S}_{\mathrm{stab}}$ lies now completely inside the demixing region.

For the present study, however, we were faced on several occasions with the situation that $\mathcal{S}_{\mathrm{stab}}$ was not inside the demixing region as α was lowered, but instead was shifted to smaller densities; thus the demixing transition could not be determined numerically. These results were confirmed both by MSA and SCOZA. From several similar cases reported in literature (see, e.g., Ref. 21) we know that if a liquid-state theory breaks down, then it is not clear whether this can be related to a complete instability of the system. Only further investigations, e.g., by using different liquid-state theories or computer simulations might lead to a conclusive decision.

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