

Reentrant miscibility in fluids with spherical interactions

N. G. Almarza,¹ E. Enciso,¹ M. F. García,¹ M. A. González,² and F. J. Bernejo³

¹*Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain*

²*Institute Laue Langevin (ILL), Boîte Postale 156, 38042 Grenoble Cedex 9, France*

³*Instituto de Estructura de la Materia, CSIC, Serrano 123, E-28006 Madrid, Spain*

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We have obtained the closed-loop fluid-fluid immiscibility in the phase diagram of a binary mixture with interactions with spherical symmetry. That topology appears when a short-range attractive interaction is considered between unlike pair molecules. We present “exact” results obtained from Monte Carlo simulation on different ensembles and results from the application of a first-order perturbation theory.

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A large number of binary fluid mixtures show immiscibility as they are cooled below an upper critical solution temperature (UCST). Less common is the reappearance of full miscibility at a lower critical solution temperature (LCST). This type of behavior has been observed in solutions of organic compounds in water or alcohols [1], and between them nicotine+water mixtures are a textbook example [2].

After some controversial discussions about the qualitative origin of such a phenomenology, Barker and Fock [3] showed the first calculations on a closed-loop phase diagram using a lattice description of mixtures with strong orientational interactions. The model was designed according to a suggestion by Hirschfelder *et al.* [4], who attributed the origin of reentrant miscibility to the freezing of the orientational entropy and the strong attraction due to hydrogen bonding, which links molecules for a few orientations. In recent years, many attempts have been made to reproduce the closed-loop shapes of actual mixtures by improving the lattice picture of the fluid [5,6]. The first successful continuum approach at predicting the closed-loop liquid immiscibility came from an application of Wertheim’s theory to symmetric hard sphere (HS) mixtures with mean-field (MF) interactions between like molecules plus a single square-well bonding site per molecule, which leads to the formation of dimers between unlike components for some molecular orientations [7].

The realm of the hydrogen bonding as the origin of the closed-loop phase diagrams arose from the failure of some earlier studies, which considered spherical interactions [8,9], to obtain reentrant miscibility. A contributing factor in that situation was the observation that the van der Waals (VDW) equation of state (EOS), combined with VDW mixing rules, can predict qualitatively almost all known phase diagram types of fluid-fluid equilibria [10]; only one type, the so-called class VI, involving a closed-loop immiscibility at low temperatures, cannot be predicted with the VDW approach. Recently, Lopes [11] has shown by computer simulation that diagrams of class VI can be found for isotropic one-center interaction potentials when the range of unlike interactions is shorter than the pure components diameter.

In this Brief Report, we revise the microscopic origin of the reentrant miscibility in fluids by considering an off-lattice model of a binary mixture with isotropic pair interac-

tions. The pair potential $u_{ij}(r)$, between molecules of species i and j is given by the square-well (SW) model:

$$u_{ij}(r) = \begin{cases} \infty & (r < \sigma_{ij}) \\ -\epsilon_{ij} & (\sigma_{ij} \leq r < \sigma_{ij}\lambda_{ij}) \\ 0 & (r > \sigma_{ij}\lambda_{ij}), \end{cases} \quad (1)$$

where r is the distance between the centers of the particles.

Models with a small number of parameters are usually better managed. This is the case of SW symmetrical mixtures, where $\sigma_{11} = \sigma_{22} = \sigma$, $\epsilon_{11} = \epsilon_{22} = \epsilon$, and $\lambda_{11} = \lambda_{22} = \lambda$. By tuning the potential parameters of the interactions between unlike particles ($\sigma_{12}, \epsilon_{12}, \lambda_{12}$), many features of the phase behavior of real systems can be observed [12–14].

In this work, the fluid phase equilibria of SW symmetrical mixtures with $\sigma_{12} = \sigma$, $\lambda_{12} \neq \lambda$, and $\epsilon_{12} \neq \epsilon$ are considered by Monte Carlo (MC) simulation and the application of the Barker and Henderson theory [15,16].

In binary mixtures, fluid phase separation can occur through two different mechanisms. Attractive interactions between particles can induce the condensation of a vapor to produce a liquid phase of higher density. On the other hand, unfavorable interactions between unlike particles can induce a demixing separation, where phases essentially differ on composition [17]. The combination of these two effects can produce very different types of phase diagrams [1]. The use of a symmetrical model makes it easier to identify the nature of different phases. The presence of demixing in a certain equilibrium between several phases of these mixtures implies that two of the phases, I and II, in equilibrium have the same density, ρ , and the mole fractions of a component, i , fulfill $x_i^I = 1 - x_i^{II}$ [14,17–19]. These two phases will be labeled “F” in the context of phase diagrams. In addition, demixing also implies the equality of the chemical potentials of both components: $\mu_1 = \mu_2$.

Simulations were performed using semi-Grand (SG) ensemble techniques [20,17], where the thermodynamic conditions are defined by the number of particles N , the temperature T , the pressure p (or the volume V), and $\mu_{12} \equiv \mu_1 - \mu_2$. Simulations were run either in one box (SG-NpT and SG-

NVT ensembles) using $\mu_{12}=0$, or in two boxes (that interchange particles and volume) using Gibbs ensemble Monte Carlo (GEMC) techniques [21] with total volume fixed.

Simulation runs are organized in cycles. In each cycle, N translations and N identity flips are attempted, one trial change of volume in SG-NpT and one attempt of volume interchange, and N attempts of particle interchange in GEMC runs. In “one-box” methods, simulations were performed using $N=108, 256, 500,$ and 864 particles. In GEMC runs, we used $N=128, 216,$ and 500 , with overall reduced density $\rho\sigma^3=0.36$.

In order to analyze the fluid demixing, an order parameter Φ is defined as $\Phi=2x-1$. The form of the probability distribution function of Φ for different systems can be monitored [18,19] by evaluating the parameter $G=(3-\langle\Phi^4\rangle)/(\langle\Phi^2\rangle^2)/2$. For given conditions of T and p (or ρ), the value of G depends on N . As N increases, G goes either to 0 (“mixed” fluid) or to 1 (“demixed” fluid). At critical conditions, G is supposed to converge rapidly with N to a non-trivial value G_c . The critical lines can be evaluated by interpolating over pairs of MC data sets with different values of N to find the conditions where G is invariant with N . We have estimated an invariant value of $G_c\approx 0.7$ in agreement with Ref. [19]. The composition of demixed phases is evaluated as $x_i=(1\pm\langle|\Phi|\rangle)/2$.

The analysis of liquid-vapor equilibrium (LVE) at a given T was performed by means of the estimation of μ using a test-particle method [22] on a number of SG-NVT simulations at different densities. The excess part of μ was fitted to a polynomial of the density. From the coefficients, we can readily evaluate the properties of the phases at equilibrium. The results were checked by performing GEMC simulations. The results of both methods agree within experimental error.

MC results can be used to test the quality of theoretical approaches. According to the first-order Barker-Henderson perturbation theory (PT) [15], the Helmholtz free energy per particle f of a binary mixture is given as

$$\frac{f(\rho, T, x_1)}{k_B T} = \frac{f_{\text{SW}}(\rho, T)}{k_B T} + \frac{\Delta f}{k_B T}, \quad (2)$$

where k_B is the Boltzmann constant, $f_{\text{SW}}(\rho, T)$ is the free energy per particle of the pure components, and Δf is the free energy of mixing per particle, which depends on T , ρ , and x_1 :

$$\frac{\Delta f}{k_B T} = \frac{x_1(1-x_1)I(\rho)}{k_B T} + x_1 \ln x_1 + (1-x_1) \ln(1-x_1). \quad (3)$$

The first term on the right-hand side corresponds to the excess free energy of mixing. $I(\rho)$ is given by

$$I(\rho) = \rho \int d\mathbf{r} g_0(\rho; r) [u_{12}(r) - u_{11}(r)], \quad (4)$$

where $g_0(\rho; r)$ is the pair distribution function of a HS fluid,

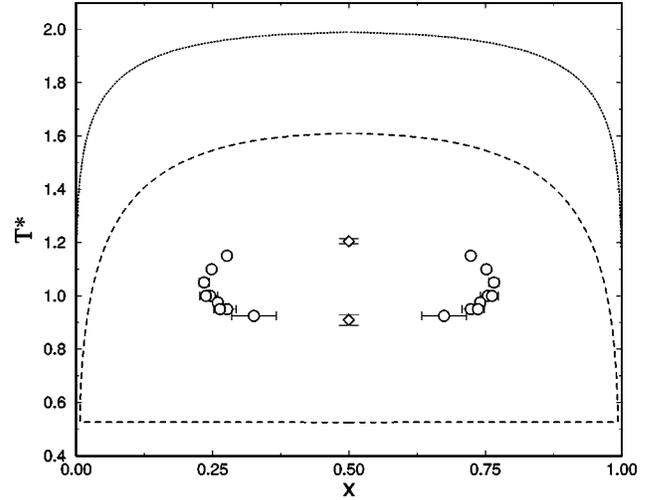


FIG. 1. The T - x phase diagram of the symmetric square well mixture with $\lambda=1.4$, $\lambda_{12}=1.1$, and $\epsilon_{12}/\epsilon=1.7$ at $p^*=1.5$. Temperatures are given in reduced units: $T^*=k_B T/\epsilon$. Dashed line shows PT results. Circles are MC results for the composition as a function of temperature, diamonds represent the estimated critical points. For comparison, we show the results for a mixture with $\epsilon_{12}=0$ (dotted line).

which is evaluated using the empirical correction of the Percus-Yevick predictions [23]. Note that the density dependence of $g_0(\rho; r)$ modifies the MF approximation underlying the VDW “ a ” parameter. In fact, such a dependence coupled with a short-range attractive potential between unlike particles can give a nonmonotonic behavior of $I(\rho)$,

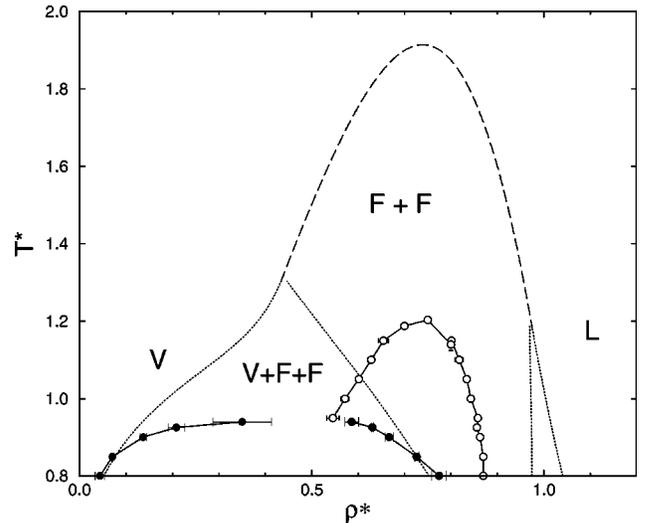


FIG. 2. T - ρ projection of the fluid phase diagram from MC and perturbation theory ($\mu_{12}=0$). Potential parameters are the same as in Fig. 1. The dashed curve represents the FFE critical line evaluated using PT. Dotted lines enclose three phase equilibria regions (evaluated with PT). Empty circles represent points on the FFE critical line evaluated from MC simulation. Filled circles correspond to the compositions of vapor and demixed fluid phases in equilibrium. Error bars are shown when the size of the symbols is exceeded. Solid lines are just joining points.

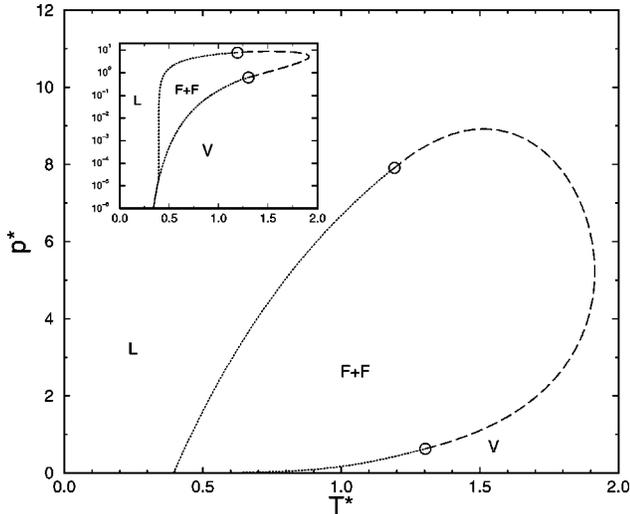


FIG. 3. p - T projection of the theoretical results on the same system shown in Fig. 2. Dashed line represents FFE critical lines. Dotted lines correspond to equilibrium between two demixed phases (FF) and a mixed fluid of either low density (V) or high density (L). Circles mark the position of tricritical points. In the inset, where pressure is given in a logarithmic scale, a quadruple point is observed at low pressure.

which produces the reentrant phenomenology. The phase equilibria of the mixtures can be evaluated within the PT approach using the following recipe. (i) Fix the values of T , μ_{12} , and a set of values of ρ . (ii) For each value of ρ , find the mole fraction of component 1, $x_1(\rho, T, \mu_{12})$, by minimizing the function $\varphi(\rho, T, x_1)$ with respect to x_1 , where $\varphi(\rho, T, x_1) \equiv f(\rho, T, x_1) - x_1 \mu_{12}$. (iii) For each density, evaluate p and μ_i as functions of T , ρ , and $x_1(\rho, T, \mu_{12})$. Discontinuous transitions on ρ (for μ_{12} constant) can be analyzed by looking for loops on the p - ρ and μ_i - ρ plots and performing Maxwell's constructions. FF equilibrium appears when $x(\rho, T, \mu_{12}=0) \neq \frac{1}{2}$. The HS contributions to the thermodynamic properties were evaluated using the Carnahan-Starling EOS [16].

In Fig. 1, we show a T - x phase diagram at reduced pressure $p^* = p\sigma^3/\epsilon = 1.5$ and $\mu_{12} = 0$ for a mixture with $\lambda = 1.4$, $\lambda_{12} = 1.1$, and $\epsilon_{12}/\epsilon = 1.7$, which shows the FF reentrant phase loop. The PT predictions show a larger immiscibility range. In addition, FF equilibrium in PT vanishes at low temperature through a first-order transition to a mixed liquid. In the same plot, we include PT results for a mixture without attractions between unlike particles ($\epsilon_{12}/\epsilon = 0$), where phase separation persists at low temperatures.

In Fig. 2, we show the T - ρ phase diagram for $\mu_{12} = 0$, given by MC calculations and PT. In Fig. 3, we show the p - T projection of the phase diagram obtained from PT. The agreement between simulation results and theory is only qualitative. At high T and p , both types of predictions show FF equilibria. The critical line of FFE, λ_{FF} , ends in the lower pressure region at the end of the line of triple points (FFV equilibrium). In PT results, this point is on the critical line of LVE defined over different values of μ_{12} . We have therefore a tricritical point (TCP). MC results seem also to indicate the

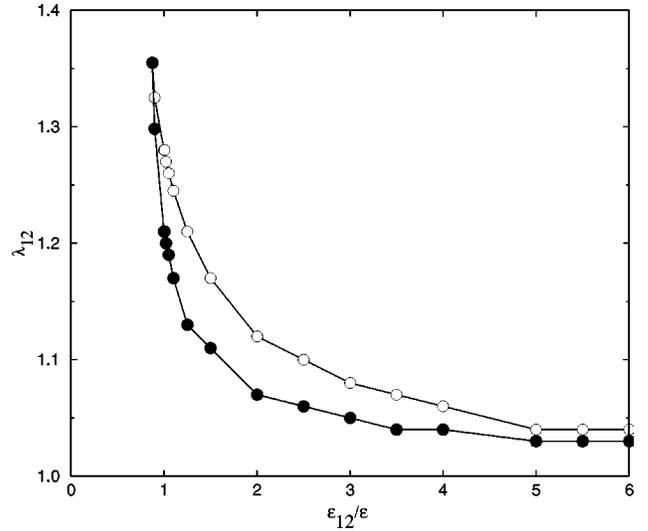


FIG. 4. Mapping of the range of the interactions between dissimilar particles that exhibit a closed-loop phase diagram, according to the predictions of perturbation theory, at $T^* = 1$ (see the text for details). Reentrant behavior appears in the region between the lines of empty and filled circles.

existence of a TCP, but the presence of LVE for $\mu_{12} = 0$ in a very small range of temperatures above T_{TCP} cannot be disregarded. The results from PT for the other end of λ_{FF} show again some peculiarity; the end point is another TCP where λ_{FF} meets a triple point line of equilibrium between demixed phases and a mixed fluid of higher density (FFLE). No evidence of this behavior was found in the range of T used in MC simulation. In any case, this high-density TCP is likely to be preempted by the solid. The presence of tricritical points in a binary mixture is due to the symmetry in the interactions [1], and it is strongly dependent on the particular values of the unlike interaction parameters.

In Fig. 4 we map the range of the dissimilar interactions (i.e., ϵ_{12} and λ_{12}) where the FF closed-loop behavior can be observed for $T^* \equiv k_B T/\epsilon = 1$ and reduced densities, $\rho^* < 1.1$. It is observed that reentrant phase behavior appears only on a small region in the space of the unlike interaction parameters, in agreement with experimental observations [24].

We have observed a closed-loop FF immiscibility in the phase diagram of a symmetric binary mixture where unlike interactions show a short-range attraction. Reentrant phases can appear in such fluid mixtures because at high densities the packing of the molecules enhances the structure of the liquid, and the miscibility of the mixture is recovered by the action of the attractive forces between unlike molecules. The VDW EOS cannot show that phenomenology, because its MF attractive parameter, with any selected combination rule, is density-independent.

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- [1] J. S. Rowlinson and F. L. Swinton, *Liquid and Liquid Mixtures*, 3rd ed. (Butterworth, Kent, 1982).
- [2] C. S. Hudson, *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **62**, 499 (1904).
- [3] J. A. Barker and W. Fock, *Discuss. Faraday Soc.* **15**, 188 (1953).
- [4] J. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.* **5**, 896 (1937).
- [5] T. Narayanan and A. Kumar, *Phys. Rep.* **249**, 135 (1994), and references therein.
- [6] J. M. Romero-Enrique, I. Rodriguez-Ponce, L. F. Rull, and U. Marini Bettolo Marconi, *Mol. Phys.* **95**, 571 (1998), and references therein.
- [7] G. Jackson, *Mol. Phys.* **72**, 1365 (1991).
- [8] J. S. Rowlinson, *Proc. R. Soc. London, Ser. A* **214**, 192 (1952).
- [9] A. Bellemans, *J. Chem. Phys.* **21**, 369 (1953).
- [10] R. L. Scott and P. H. van Konynenburg, *Discuss. Faraday Soc.* **49**, 87 (1970); P. H. van Konynenburg, Ph.D. thesis, University of California, Los Angeles, 1968.
- [11] J. N. C. Lopes, *Mol. Phys.* **96**, 1649 (1999).
- [12] J. R. Recht and A. Z. Panagiotopoulos, *Mol. Phys.* **80**, 843 (1993).
- [13] G. Jackson, *Mol. Phys.* **72**, 1365 (1991); D. R. Green, G. Jackson, E. de Miguel, and L. F. Rull, *J. Chem. Phys.* **101**, 3190 (1994); E. de Miguel, E. M. del Rio, and M. M. Telo da Gama, *ibid.* **103**, 6188 (1995).
- [14] N. B. Wilding, F. Schmid, and P. Nielaba, *Phys. Rev. E* **58**, 2201 (1998).
- [15] J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
- [16] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, New York, 1986).
- [17] E. Lomba, M. Alvarez, L. L. Lee, and N. G. Almarza, *J. Chem. Phys.* **104**, 4180 (1996).
- [18] N. B. Wilding and P. Nielaba, *Phys. Rev. E* **53**, 926 (1996).
- [19] N. B. Wilding, *Phys. Rev. E* **55**, 6624 (1997).
- [20] D. A. Kofke and E. D. Glandt, *Mol. Phys.* **64**, 1105 (1988).
- [21] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, San Diego, 1996).
- [22] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
- [23] W. R. Smith and D. Henderson, *Mol. Phys.* **19**, 411 (1970); L. Verlet and J. J. Weis, *Phys. Rev. A* **2**, 939 (1972).
- [24] I. V. Brovchenko and A. V. Oleinikova, *J. Chem. Phys.* **106**, 7756 (1997). The authors speculate about the range of interactions as the main factor that can explain that β -picoline + heavy water mixtures show reentrant miscibility but β -picoline + water mixtures do not show that phenomenology.