On the phase separation of a binary fluid in a porous medium

E. Paschinger[1,2], D. Levesque[2], G. Kahl[1] and J.-J. Weis[2]

[1] *Institut für Theoretische Physik and Center for Computational Materials Science*
TU Wien - Wiedner Hauptstraße 8-10, A-1040 Wien, Austria
[2] *Laboratoire de Physique Théorique, UMR 8627, Bât. 210, Université de Paris-Sud*
F-91405 Orsay Cedex, France

Abstract. – Our investigations of the phase diagram of a symmetric binary fluid in equilibrium with a porous matrix show that moderate changes in the properties of the matrix or in the matrix-fluid interaction lead to drastic modifications of the phase diagram of the fluid. Thus our results confirm on a qualitative basis recent experimental data. The phase diagrams that we have obtained show a wide variation and can be classified in terms of archetypes of systems of two order parameters. These different types can be characterised in terms of the loci where the λ-line of the demixing transition intersects the first-order liquid-vapour coexistence curve. Results are based on the optimised random phase approximation and on grand-canonical Monte Carlo simulations.

Introduction. – Investigations of the properties of fluids in equilibrium with a disordered structure (matrix) have become during the past years a very challenging field in liquid-state physics [1]. Experimental and theoretical studies revealed that a porous matrix (even if it occupies only a small fraction of the volume) can have a substantial influence on the phase behaviour of the liquid: ^{4}He and N_2 in high-porosity aerogel [2] are two examples where the near-critical liquid-vapour (LV) curve is narrowed drastically under the influence of a matrix. The effects become of course more rich and interesting in the case that the fluid is a binary mixture: for example, experiments on a ^{3}He-^{4}He mixture inside a highly porous silica-gel or a porous gold matrix have shown a drastic modification of the superfluid transition [3]. A deeper understanding of these obviously very complex effects is all the more desirable as it might help to predict properties of materials of technological relevance with widespread applications in catalysis, adsorption, etc. In this perspective the study of a simple model of a binary fluid which mimics characteristic features of the matrix-fluid and fluid-fluid interaction of realistic systems can give important information of how the variation of these interactions modifies the phase behaviour of the system. We consider here a symmetric binary hard-core Yukawa mixture in a porous matrix: *i.e.* the like-particle interactions of the fluid particles

and the fluid-matrix interactions are identical for both components, while the interactions between unlike fluid particles differ from the like ones. We present here the first systematic investigations of the influence of the system parameters of these systems on the phase diagram.

The phase behavior of a pure binary symmetric mixture (even without the matrix) already shows a very wide variation, which is induced by the competition between fluid demixing and LV transition. In a recent mean-field study, Wilding *et al.* [4] showed that three different types of phase diagrams occur, according to the loci where the λ-line (critical line of the fluid demixing) intersects the LV curve: in type I a critical end point (CEP) behaviour is observed, in type II one encounters a triple point (a vapour and two liquids of different densities) and a tricritical point, and type III is characterised by a tricritical point and the absence of vapour-mixed fluid transition. The change I $\rightarrow$ II $\rightarrow$ III is shown to be induced by decreasing the ratio between the unlike and the like interactions.

If the symmetric binary liquid mentioned above is now brought into thermal equilibrium with a porous matrix, similar phase diagrams (type I to III) are observed, as the parameters of the *fluid-fluid* particle interactions are varied, in qualitative agreement with those results presented for the pure binary liquid [4]. However, and this will be shown in the present contribution, the variation of the properties of the *matrix* and of the *matrix-fluid* particle interactions, keeping the potential between the *fluid* particles fixed, also is able to induce trends in phase diagrams similar to the ones outlined above. A Monte Carlo study based on the Gibbs ensemble simulation method for the phase behaviour of a symmetric binary Lennard-Jones fluid has been presented previously by Gordon and Glandt [5] but was restricted to the investigation of the liquid-liquid transition.

Model, theory and simulations. – A binary liquid inside a porous matrix can be considered as a very special three-component liquid, where the particles of the matrix are fixed in place and are not affected by the mobile particles of the liquid. Physical quantities are hence obtained by two successive averages: a first average taken over the degrees of freedom of the fluid particles (keeping the positions of the matrix particles fixed) and a second one over all possible degrees of freedom of the matrix particles. Perhaps the most promising approach to solve this problem has been proposed by Given and Stell [6] who have introduced the replica trick in this field: it exploits an isomorphism between the partly quenched and a fully equilibrated system which consists of the now mobile matrix particles and of s noninteracting identical copies of the liquid; the properties of the quenched system are obtained by considering the limit $s \rightarrow 0$ of the equilibrium system, which, in turn, can be treated by standard liquid-state theories. Using this framework, nine Ornstein-Zernike–type integral equations [7] (so-called replica Ornstein-Zernike equations —ROZ) can be derived that relate the direct and total correlation functions of the fluid and matrix particles; one of these equations describes the matrix correlation functions and is decoupled from the other equations. The remaining eight equations are coupled and have to be solved along with a closure relation.

The system we have studied is a symmetric binary Yukawa mixture in equilibrium with a porous matrix. The full set of interactions can be written as hard-sphere Yukawa potentials ($\beta = 1/(k_{\mathrm{B}}T)$)

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

Index 0 denotes the matrix particles, while 1 and 2 denote the two components of the liquid. The diameter σ is assumed to be equal for all interactions and is put to unity; the contact values K_{ij} are parameterised as follows: $K_{00} = 0$, $K_{11} = K_{22}$, $K_{12} = \alpha K_{11}$, $K_{01} = K_{02} = yK_{11}$; $T^{\star} = \sigma/K_{11}$. Further system parameters are the concentration of species 1 of the fluid, x, the

fluid density $\rho_{\mathrm{f}} = \rho_1 + \rho_2$ and the matrix density ρ_{m}. In all calculations presented here $z\sigma$ was assumed to be 2.5 and the potentials have been truncated at 2.5σ (both in the simulations and the theoretical calculations). Densities ρ_{α} are in units of σ^3.

The theoretical results stem from a thermodynamic perturbation theory where the interatomic potentials are split into a reference and a perturbation part. For the hard-sphere reference system we have solved the ROZ equations along with the Percus-Yevick closure relation; corrections due to the perturbation (Yukawa tails) are treated in the optimised random phase approximation (ORPA) [8]. The formalism and details for the numerical solution are given in [7]. The chemical potentials and the pressure are calculated for the reference system via a numerical integration of the compressibility equation. For the excess parts of these thermodynamic quantities we have derived in [7] closed expressions valid in the ORPA. We have determined the phase diagrams by equating, at a given temperature T, the pressure P and the chemical potentials μ_1, μ_2 of the coexisting phases (homogeneous vapour V, homogeneous mixed fluid MF, and demixed fluid DF). The V-MF coexistence is obtained by solving the set of equations

$$\mu_i(\rho_{\mathrm{f}}, x = 1/2) \equiv \mu(\rho_{\mathrm{f}}, x = 1/2) = \mu(\rho_{\mathrm{f}}', x = 1/2)\,, \tag{2}$$

$$P(\rho_{\mathrm{f}}, x = 1/2) = P(\rho_{\mathrm{f}}', x = 1/2)\,. \tag{3}$$

For the V-DF transition we proceed in two steps: first we determine the phase diagram of the demixing transition by equating

$$\mu_1(\rho_{\mathrm{f}}, x) = \mu_2(\rho_{\mathrm{f}}, x), \tag{4}$$

yielding the demixing transition line $x(\rho_{\mathrm{f}})$. In a second step we solve

$$\mu(\rho_{\mathrm{f}}, x = 1/2) \;=\; \mu(\rho_{\mathrm{f}}', x(\rho_{\mathrm{f}}'))\,, \tag{5}$$

$$P(\rho_{\mathrm{f}}, x = 1/2) \;=\; P(\rho_{\mathrm{f}}', x(\rho_{\mathrm{f}}'))\,. \tag{6}$$

In the Monte Carlo (MC) simulations we consider both the bulk fluid mixture and the same mixture in a porous matrix obtained from a frozen hard-sphere configuration. The volume of the simulation cell with periodic boundary conditions is $500\sigma^3$. The configurations of the fluid particles in the matrix have been generated according to the grand-canonical distribution, the identity of the 11 and 22 interactions implying the chemical potentials of the two species to be equal. A thermodynamic state of the pure mixture or of the mixture adsorbed in the matrix depends therefore only on the chemical potential $\mu = \mu_1 = \mu_2$ and T. The calculations are performed by determining, for fixed μ and T, the equilibrium states of the mixture for a series of matrix configurations typical of the canonical ensemble of hard spheres. The quantities calculated, in particular the joint probability $p(u, n_1, n_2, T, \mu)$ for a configuration of molecules in the mixture to have internal energy u and species numbers n_1 and n_2, are evaluated by an average of the results obtained for each matrix configuration. The distributions $p(u, n_1, n_2, T, \mu)$ obtained, for a given matrix density, at different values of μ are used, within the framework of a reweighting procedure [9,10], to determine the mean density ρ_{f} and the average compositions $x_1 = \langle n_1 \rangle / \langle n_1 + n_2 \rangle$ and $x_2 = 1 - x_1$ along an isotherm.

Phase equilibria corresponding to first-order transitions, V-MF, V-DF or MF-DF, are located by determining, by means of reweighting, the chemical potentials giving peaks of equal heights in $p(u, n_1, n_2, T, \mu)$ for two values of $\rho_{\mathrm{f}} = \langle n_1 + n_2 \rangle / V$ with either $n_1 = n_2$ for both densities or $n_1 = n_2$ for one density and $n_1 \neq n_2$ for the other. Second-order phase transitions were identified by calculating from $p(u, n_1, n_2, T, \mu)$ the distribution $p_{\mathrm{d}}(u, n_1 -$

n_2, T, μ) and determining the value of ρ_f at which the peak at $p_d(u, 0, T, \mu)$ corresponding to the homogeneous phase progressively splits into two peaks symmetric with respect to the origin. Typical simulations of the pure mixture involve 10^8 trial MC moves (displacement, insertion or deletion of a molecule). In the presence of the matrix, for each configuration of the latter, 10^8 trial MC moves are carried out to estimate the equilibrium state of the mixture; the results obtained for these equilibrium states are then averaged over 6 to 50 configurations of the matrix depending on whether the equilibrium state of the fluid is a homogeneous or demixed state or whether one is close or not to a phase transition. The relative precision of ρ_f, x_1 and x_2 is of the order of 2-3%; similarly, the values of μ at the transitions obtained by reweighting have a precision of 1-2%.

Results. – In fig. 1 we compare simulation data and ORPA results for three systems with matrix density $\rho_m = 0$ (pure binary liquid), $\rho_m = 0.05$ and $\rho_m = 0.15$; α is set to 0.7 and $y = 1$. In all three cases we find a type-II phase diagram characterised by a tricritical point at a temperature T_{tc}, where the λ-line of the second-order demixing transition terminates. Further, we observe a triple point T_{tr} where a vapour, a MF and a DF (of higher density) coexist. As we increase the matrix density, the difference between T_{tc} and T_{tr} decreases; at $\rho_m \sim 0.30$ (not shown here) the first-order transition between the MF and the DF vanishes, leading to a CEP at T_{cep} (type-I diagram). The CEP causes a kink in the LV curve, which is clearly visible in the ORPA curves; this phenomenon has been discussed for a pure mixture in [11]. These results show that a moderate matrix density is able to suppress completely a first-order transition between a mixed and a demixed fluid.

In the ORPA the regions near the LV critical point and the tricritical point are difficult to access due to the fact that the coupled equations (2), (3), (5) and (6) become ill-conditioned and do not allow an accurate location of the critical temperature and density. Estimates for the LV critical points, given in the caption of fig. 1, have been made using a simple scaling law and the law of rectilinear diameters. In view of the fact that the ORPA is just a mean-spherical–type approximation, the agreement between simulation results and numerical calculations is very satisfactory in the pure case. Similar good agreement also holds for the case $\alpha = 0.9$. Here the λ-line has disappeared both in the simulations and the ORPA. Agreement becomes less good as we increase the matrix density. For the highest matrix density shown ($\rho_m = 0.15$) the ORPA and simulation estimates of the critical temperatures differ by $\sim 4\%$. The main discrepancies occur on the vapour side of the V-MF and V-DF transitions. Furthermore, one observes a systematic shift of the ORPA estimate of the λ-line towards lower densities.

The strong influence of the matrix on the phase behaviour of the liquid becomes even more evident if we vary the matrix-fluid particle interaction (cf. fig. 2). Changing this interaction from attraction ($y = 3.5$) to repulsion ($y = -1$), we observe for the matrix density $\rho_m = 0.05$ that the V-MF transition occurs only in a limited region ($y \sim -0.5$ to $y \sim 2$). We encounter the following sequence of types of phase diagrams: III at $y = 3.5$, II/III at $y = 2$ (here the numerical difficulties mentioned above do not allow to make a clear decision which type is realized), II at $y = 1$ (cf. fig. 1) and $y = 0$, and finally III at $y = -1$. This sequence leads to the conclusion that a strongly attractive or a repulsive matrix suppresses the existence of the mixed liquid.

Turning off the attractive tail for the matrix-liquid interaction (by choosing $y = 0$) leads to a completely new sequence for different values of the matrix density than in the case $y = 1$: the phase diagram of the pure fluid is of type II and turns into type III at rather low matrix densities. A more detailed analysis of our results will be presented in a future contribution.

In contrast to the Heisenberg fluid [12], the Stockmayer fluid [13] and the pure binary symmetric liquid [4] where only one parameter triggers the transition from one type of diagram
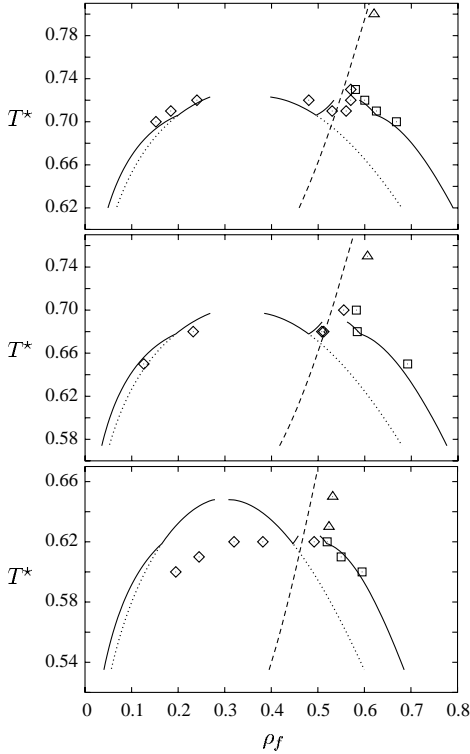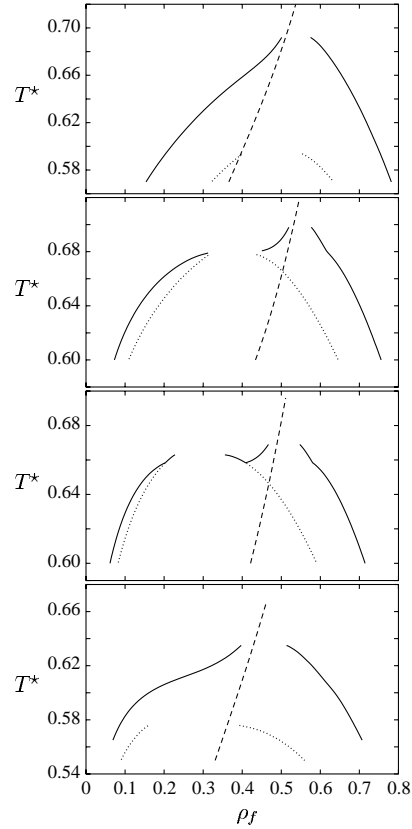
Fig. 1

Fig. 2

Fig. 1 – Phase diagram of a binary symmetric Yukawa mixture in thermal equilibrium with a porous matrix ($\alpha = 0.7$, $z\sigma = 2.5$, and $y = 1$): $T^\star$ vs. ρ_f (in units of σ^3); for $\rho_m = 0$, 0.05, and 0.15 (from top to bottom). Symbols: grand-canonical MC simulations (diamond: V, MF; square: DF; triangle: λ-line), lines: ORPA results (full line: coexistence curve; dotted line: metastable V-MF transitions; dashed line: λ-line); ORPA estimates for (T_c, ρ_c) from top to bottom: (0.726, 0.34); (0.700, 0.33); (0.649, 0.30).

Fig. 2 – Phase diagram of a binary symmetric Yukawa mixture in thermal equilibrium with a porous matrix ($\alpha = 0.7$, $z\sigma = 2.5$, and $\rho_m = 0.05$): $T^\star$ vs. ρ_f (in units of σ^3); variation of y (from top to bottom: $y = 3.5$, 2, 0, -1). ORPA results: symbols as in fig. 1.

to the other, we have to deal in the present case with 3 parameters (ρ_m, α, y) each of which can trigger the system from one type to another. In particular we point out that already moderate or even small modifications of these parameters are able to induce drastic effects in the phase diagram of the liquid; hence the strong modifications of the phase behaviour of liquids in the presence of a porous matrix observed in experiment are not too surprising.

The comparison of the theoretical and simulation results shows that the ORPA allows for a nearly quantitative prediction of the phase diagram of a binary mixture in a disordered medium even of low porosity. Moreover, its use establishes that the variation of phase diagrams, in particular the existence of V-MF transition, results from a complex interplay between the parameters governing the fluid-fluid and matrix-fluid interactions.

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