Phase diagrams of a fluid confined in a disordered porous material

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Abstract. We present the calculation of phase diagrams for a single-component fluid adsorbed in disordered porous material using integral equation theories. The model consists of a Lennard-Jones 12–6 fluid confined in a rigid matrix of spheres. In most cases a vapour–liquid coexistence curve is obtained. It is similar to that observed for the bulk fluid although displaced towards the phase that adsorbs preferentially. The ORPA + B_2 approximation also predicts the appearance of a second fluid–fluid phase transition at low temperature that may be consistent with the narrowing of the coexistence curve observed in experiments.

1. Introduction

The phase behaviour of fluids and fluid mixtures in disordered porous materials has been recently the focus of much interest both from an experimental and a theoretical perspective [1]. The systems studied include fluid mixtures in porous glasses as well as both single-component fluids and fluid mixtures in dilute silica networks. There is now strong evidence that fluids in porous media, at least in dilute gels, undergo true phase transitions, albeit with features strikingly different from those of bulk fluids. Thus, the phase diagrams of ^{4}He and N_2 in aerogels show, compared to the bulk case, a remarkable narrowing of the liquid–vapour coexistence curve and a displacement of the critical point to a lower temperature and higher density [2]. Neither explanations that totally neglect the effect of randomness of the pore network [3] nor interpretations in terms of the random-field Ising model (RFIM) [4], where confinement plays no role, seem to be sufficient to describe all the observed behaviours.

On the other hand, an approach that embodies confinement, randomness, and connectivity of the pore network altogether has emerged recently through adaptation of ideas from liquid-state statistical mechanics [5]. In this approach the system is modelled as a so-called 'quenched–annealed' binary mixture in which the fluid molecules equilibrate in a matrix of particles frozen in a disordered configuration. This latter configuration is sampled from an equilibrium ensemble where the matrix particles interact via some specified potential in the absence of the fluid. Many techniques from liquid-state statistical mechanics can be extended to this problem by using the replica trick [6, 7]. The present paper is concerned with the application of these ideas to the prediction of phase equilibrium for fluids in disordered porous materials.

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2. Theory

The starting point of our calculations is a set of coupled integral equations which relate the total pair correlation functions $h_{\alpha\beta}(r)$ of the quenched–annealed mixture to the corresponding direct correlation functions $c_{\alpha\beta}(r)$. The exact form of these equations is most easily derived by using the replica method [6] which replaces the study of the original system by that of an equilibrium mixture composed of the matrix particles and s identical copies (or replicas) of the fluid particles. The s fluid replicas do not interact with each other but they interact with the matrix. This set of coupled integral equations, called hereafter the replica-symmetric Ornstein–Zernike (RSOZ) equations, is obtained by taking the limit $s \to 0$ of the corresponding set in the replica space. One finds

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \tag{1a}$$

$$h_{10} = c_{10} + \rho_0 c_{10} \otimes h_{00} + \rho_1 c_c \otimes h_{10} \tag{1b}$$

$$h_{11} = c_{11} + \rho_0 c_{10} \otimes h_{01} + \rho_1 c_c \otimes h_{11} + \rho_1 c_b \otimes h_c \tag{1c}$$

$$h_c = c_c + \rho_1 c_c \otimes h_c \tag{1d}$$

where the explicit dependence on r has been dropped for notational simplicity and the symbol $\otimes$ denotes a convolution in $\boldsymbol{r}$-space. ρ_α is the average density of species i ($\alpha = 0$ for the matrix, $\alpha = 1$ for the fluid). h_b, c_b, $h_c \equiv h_{11} - h_b$, and $c_c \equiv c_{11} - c_b$ are the so-called blocking (or disconnected) part and connected part of h_{11} and c_{11}. As shown in reference [7], the connected and blocking parts of h_{11} correspond to the following averaged quantities:

$$\rho_1^2 h_c(r_{12}) = \overline{\rho_{11}^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{q}^{N_0}) - \rho_1(\boldsymbol{r}_1; \boldsymbol{q}^{N_0})\rho_1(\boldsymbol{r}_2; \boldsymbol{q}^{N_0})} \tag{2}$$

and

$$\rho_1^2 h_b(r_{12}) = \overline{\rho_1(\boldsymbol{r}_1; \boldsymbol{q}^{N_0})\rho_1(\boldsymbol{r}_2; \boldsymbol{q}^{N_0})} - \rho_1^2 \tag{3}$$

where $\rho_1(\boldsymbol{r}_1; \boldsymbol{q}^{N_0})$ and $\rho_{11}^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{q}^{N_0})$ are, respectively, the one- and two-particle densities of the fluid in a particular realization of the matrix in which N_0 matrix particles occupy positions $\boldsymbol{q}^{N_0} = (\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_{N_0})$ and the overbar represents the average over matrix realizations.

The thermodynamics of quenched–annealed systems has been discussed in references [7] and [8]. In particular, it has been shown that the grand potential density satisfies the Gibbs–Duhem relation but is not equal to the mechanical pressure that is obtained by averaging the stress tensor over matrix realizations. The thermodynamics can be computed directly from the pair correlation functions using either the compressibility or the energy route. Although the virial equation contains unusual terms, it is also a possible route to thermodynamics, as shown recently [9].

One needs as usual closure relations to solve the RSOZ equations and derive the thermodynamics. One first writes a closure for the $(s + 1)$-component 'replicated' mixture and then takes the limit $s \to 0$. We propose here to use theories such as the optimized random-phase approximation (ORPA) and the optimized cluster theory (OCT) [10] which give an accurate treatment of correlation functions and vapour–liquid coexistence for bulk fluids. Moreover, in ORPA and OCT, closed-form expressions of the free energy can be derived. For instance, assuming that all pair interactions in the quenched–annealed mixture comprise a reference hard-sphere part and an attractive perturbation $u_{\alpha\beta}$, the ORPA free energy can be written as [11]

$$\overline{\mathcal{A}}^{ORPA} = \overline{\mathcal{A}}^R + \frac{1}{2}[\rho_1^2(\hat{c}_c(0) - \hat{c}_c^R(0)) + \rho_1 \rho_0(\hat{c}_{10}(0) - \hat{c}_{10}^R(0))] - \frac{\rho_1}{2}[c_{11}(0) - c_{11}^R(0)]$$

$$- \frac{1}{2(2\pi^3)} \int d\mathbf{k} \ \ln \frac{1 - \rho_1 \hat{c}_c(k)}{1 - \rho_1 \hat{c}_c^R(k)} - \beta \frac{\rho_1 \rho_0}{2} \int d\mathbf{r} \ g_{01}(r) u_{01}(r)$$

$$+ \frac{\rho_1^2}{2} \int d\mathbf{r} \ [h_c(r) - h_c^R(r)] c_b^R(r) + \frac{\rho_1 \rho_0}{2} \int d\mathbf{r} \ [h_{01}(r) - h_{01}^R(r)] c_{01}^R(r)$$

$$(4)$$

where R denotes a quantity in the reference system and the caret denotes the Fourier transform of a function.

The mean-spherical approximation (MSA) is obtained from the ORPA by replacing the exact reference correlation functions by their Percus–Yevick counterparts. An interesting feature is that one can then derive a closed-form expression for the excess chemical potential of the fluid [11]. One can also derive the EXP (exponential) approximation for the correlation functions and the corresponding 'ORPA + B$_2$' approximation for the free energy by summing additional diagrams in the OCT.

It should be noted that none of these theories is thermodynamically self-consistent in the sense that the isothermal compressibility χ obtained from the above expressions of the free energy differs from the one given by the compressibility equation. As discussed in reference [12], the compressibility route does not yield a critical point when $d \leqslant 4$ in such Ornstein–Zernike theories. This not the case when using the energy route, and one then obtains classical mean-field behaviour at criticality.
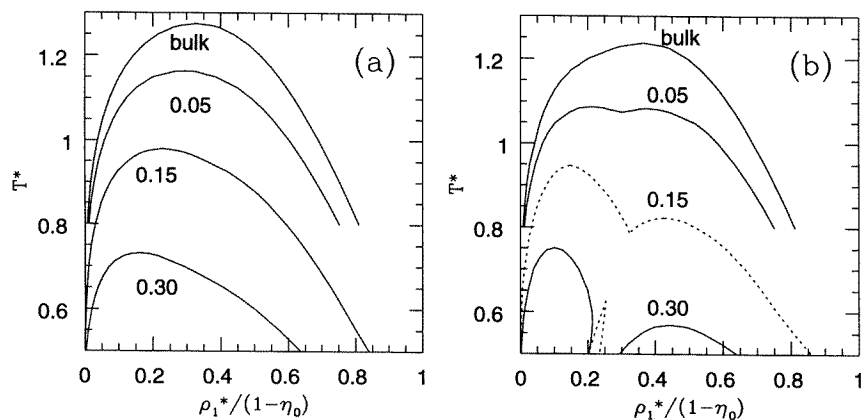

Figure 1. Portions of coexistence envelopes for a completely repulsive fluid–matrix interaction ($y = 0$). Each curve is labelled with the corresponding value of the reduced matrix density ρ_0^*. (a) Predictions of the MSA. (b) Predictions of the ORPA + B$_2$ theory.

3. Results for a model system

The model consists of a fluid of spherical molecules confined in matrices of spheres described by equilibrium hard-sphere (EHS) configurations. The matrix–fluid and fluid–fluid interactions decompose into a hard-sphere part and a Lennard-Jones 12–6 tail *à la* Weeks–Chandler–Andersen, i.e., $u_{\alpha\beta}(r) = -\epsilon_{\alpha\beta}$ for $\sigma_{\alpha\beta} < r < 2^{1/6}\sigma_{\alpha\beta}$ and $u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$ for $r > 2^{1/6}\sigma_{\alpha\beta}$. This defines the interaction ratio $y = \epsilon_{01}/\epsilon_{11}$. In order to make contact with a recent MSA calculation for a lattice-gas version of a fluid in a disordered matrix [13], we consider a system in which $\sigma_{01} = \sigma_{11} = \sigma$. Moreover the

Lennard-Jones tails are cut at $r/\sigma = 2.5$. In all calculations, the reference system correlation functions are obtained by solving the RSOZ equations in the Percus–Yevick approximation and the pressure and chemical potential of the reference system are calculated by integration of the compressibility equation of state.

Figure 1(a) shows examples of coexistence envelopes in the case of a (completely repulsive) hard–sphere fluid-matrix interaction ($y = 0$) obtained with MSA at the reduced densities $\rho_0^* = \rho_0\sigma^3 = 0$ (bulk), 0.05, 0.15, and 0.30 ($T^* = kT/\varepsilon_{11}$ and the reduced fluid densities $\rho_1^* = \rho_1\sigma^3$ have been renormalized by the matrix porosity $\phi = 1 - \eta_0$, where $\eta_0 = \pi/6\rho_0^*$). One sees a displacement of the critical point to lower temperature and to lower density as one increases the matrix density. The critical-point suppression with increasing confinement is also predicted by simple mean-field calculations [14]. The corresponding phase diagrams obtained with the ORPA $+$ B$_2$ theory are shown in figure 1(b). Surprisingly, they look quite different: as the density of the matrix increases, a shoulder appears on the high-density side of the vapour–liquid coexistence region and this shoulder gives rise very soon to a second coexistence region at lower temperature. Such a pre-evaporation transition has been observed in the recent Monte Carlo simulations of Page and Monson [15] in which the matrix particles are seven times larger than the fluid molecules. It corresponds to an expulsion of the fluid from the regions where the matrix is more dense. The MSA solution of the quenched–annealed lattice-gas model [13] also predicts the occurrence of this transition when the fluid–matrix interaction becomes sufficiently repulsive.
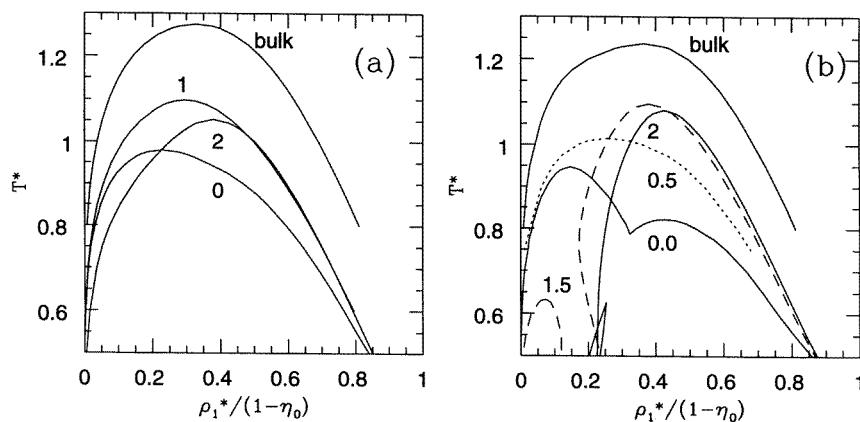

Figure 2. Portions of coexistence envelopes as a function of the interaction ratio y for a matrix with reduced density $\rho_0^* = 0.15$. Each curve is labelled with the corresponding value of y. (a) Predictions of the MSA. (b) Predictions of the ORPA $+$ B$_2$ theory.

Next we consider the case of attractive fluid–matrix interactions. Figure 2(a) shows coexistence envelopes obtained with MSA as one varies the interaction ratio y while keeping the density of the matrix equal to $\rho_0^* = 0.15$. It is seen that the variations of the critical temperature with y are non-monotonic: T_c first increases and then decreases as one increases y. On the other hand, the critical density increases monotonically and becomes larger than the bulk value as observed in the experiments on aerogel [2]. Simple mean-field theories [14] are unable to predict such features. The predictions of the ORPA $+$ B$_2$ theory shown in figure 2(b) are again more complicated. As y increases, the second coexistence region first disappears, then reappears on the vapour side at low temperature and is finally displaced to temperatures below $T^* = 0.5$. There is also a significant narrowing of the coexistence

curve compared to the bulk one, although this effect seems smaller than in the experiments [2]. A second transition on the low-density side of the vapour–liquid coexistence region has been also found in Monte Carlo simulations [15] and in the MSA treatment of the lattice-gas model [13]. The appearance of a second critical point is also predicted by a recent calculation for an array of cylindrical strands [16]. In this case, however, it is attributed to fluctuation-induced effects.

Finally, it should be noted that inclusion of next-order terms in the OCT expansion of the free energy changes the overall picture again (the second transition does not exist any more). This convergence problem in the theory can be traced back to the large values reached by the renormalized potentials in the intermediate-density region. Such a problem does not exist for bulk fluids where these densities correspond to the two-phase region and only one van der Waals loop is expected.

4. Conclusion

We have presented a liquid-state formalism applicable to fluids in disordered porous media. Although the model for the matrix is unable to represent realistic dilute silica gels, our study using integral equations shows an interesting phase behaviour that may be consistent with experimental results. In particular, some of our results suggest that the narrowing of the coexistence curve may be related to the occurrence of a second phase transition at lower temperatures. However, our predictions are sensitive to the approximation and, contrary to the bulk case, the description of the phase behaviour of fluids in disordered porous media appears to depend critically on the intermediate-density region.

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