PHYSICAL REVIEW E, VOLUME 64, 042101

Effect of templated quenched disorder on fluid phase equilibrium

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(Received 9 January 2001; published 17 September 2001)

Templating offers a means to direct the structure of quenched disorder. We show here that changes in phase equilibrium due to the presence of quenched disorder can themselves be altered by templating. We calculate the phase diagram of a fluid in a collection of template-directed, quenched particles by solving a set of replica Ornstein-Zernike equations within the mean spherical approximation and show templating to enhance phase behavior, that is, shift the phase envelope upward from its location for a nontemplated system of identical available volume. This enhancement is due to an augmented number of fluid-fluid interactions.

DOI: 10.1103/PhysRevE.64.042101 PACS number(s): 05.20.Jj, 61.20.Gy, 64.70.Fx, 81.05.Rm

The presence of quenched disorder is known to have a profound effect on the phase behavior of various magnetic and fluid systems [1]. Examples of this are single component or binary systems immersed in porous glasses or silica gels [2–9]. In these systems, the liquid-vapor or liquid-liquid critical temperature is typically lowered and the phase envelope narrowed compared to those of the corresponding bulk system. Although the effects of quenched disorder are often explained by the presence of random fields in a fully available system [10], most physical manifestations involve highly correlated fields and regions of unavailability (due to, for example, gel strands or pore walls). It is clear that these characteristics, and thus also the nature of any phase transition, depend on the structure of the quenched disorder, a property that can be controlled by realizing the quench in the presence of a removable, structure-directing template. An important practical example of this is the molecular templating of porous materials where the material is formed (perhaps by gelation) in the presence of a shape-directing template species that is later removed by thermal or chemical treatment [11]. Ideally, the material's structure will mimic, to some extent, the structure of the template. Templated porous materials find use as adsorbents, sensors, gas separation membranes, and molecular recognition agents. One can envision using templating, together with existing methods for controlling porosity, to tailor porous materials that impart a specific phase behavior to an adsorbed fluid.

In this paper, we investigate fluid phase behavior in the presence of templated quenched disorder. We model both the fluid and the quenched disorder in terms of discrete particles; the latter being a quenched, equilibrated configuration of a binary mixture of ''matrix'' and ''template'' particles with the template component removed [12]. The analogy between the construction of this model and the formation of a templated porous material is obvious, but the model may also apply more generally to systems containing perturbed quenched randomness, such as certain alloys, glasses, and magnetic systems.

Simulation [13,14] and liquid-state theory [15,16] have shown that the temperature-density phase envelope of a fluid immersed in a collection of quenched particles is lowered with increasing number density of the matrix. It is also observed experimentally [11] and theoretically [12] that templating increases the volume available to an adsorbed fluid, so one might expect templating to have an effect similar to decreasing the quenched matrix number density. It is one of the goals of this article to distinguish these two effects.

Using arguments similar to ones used for nontemplated systems [17,18], we recently proposed a set of replica Ornstein-Zernike equations relating the direct and total correlation functions for a fluid in a templated porous material [19]:

$$h_{00}=c_{00}+\rho_0 c_{00}\otimes h_{00}+\rho_{0'}c_{00'}\otimes h_{00'}, \tag{1}$$

$$h_{00'}=c_{00'}+\rho_0 c_{00}\otimes h_{00'}+\rho_{0'}c_{00'}\otimes h_{0'0'}, \tag{2}$$

$$h_{0'0'}=c_{0'0'}+\rho_0 c_{00'}\otimes h_{00'}+\rho_{0'}c_{0'0'}\otimes h_{0'0'}, \tag{3}$$

$$h_{01}=c_{01}+\rho_0 c_{00}\otimes h_{01}+\rho_{0'}c_{00'}\otimes h_{0'1}+\rho_1 c_{01}\otimes h_c, \tag{4}$$

$$h_{0'1}=c_{0'1}+\rho_0 c_{00'}\otimes h_{01}+\rho_{0'}c_{0'0'}\otimes h_{0'1}+\rho_1 c_{0'1}\otimes h_c, \tag{5}$$

$$h_{11}=c_{11}+\rho_0 c_{01}\otimes h_{01}+\rho_{0'}c_{0'1}\otimes h_{0'1}+\rho_1 c_c\otimes h_{11}+\rho_1 c_b \otimes h_c, \tag{6}$$

$$h_c=c_c+\rho_1 c_c\otimes h_c, \tag{7}$$

where c_{ij} (h_{ij}) is the direct (total) correlation function between components i and j, ρ_i is the density of component i, $\otimes$ is a convolution, and the subscripts 0, $0'$, and 1 are the matrix, template, and fluid components, respectively. In addition, h_c and c_c are the ''connected'' parts of the correlation functions, defined as the sums of contributing diagrams possessing at least one path connecting the fluid root points and not passing through any matrix field points [17,18].

We restrict ourselves to spherically symmetric potentials divisible into a hard core repulsion and an attractive tail perturbation. We employ the mean spherical approximation [20] to solve Eqs. (1)–(7): $h_{ij}(r)=-1$ for $r<\sigma_{ij}$ and $c_{ij}(r)=$

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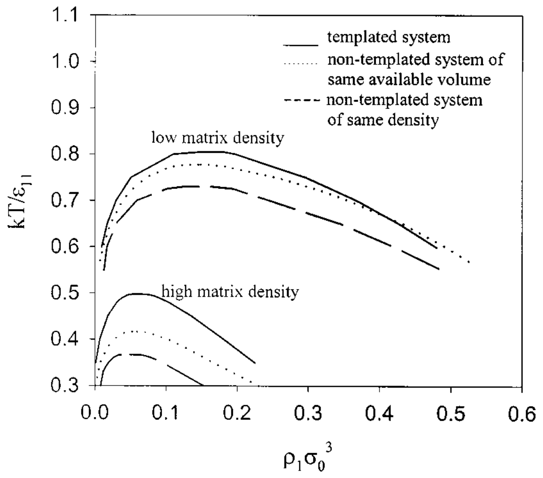

FIG. 1. Liquid-vapor phase envelopes for a fluid in (from top to bottom in each threesome) a system of templated quenched particles, a system of nontemplated quenched particles of the same available volume (but lower density), and a system of nontemplated quenched particles of the same density as the top curve. The matrix and template densities, from top to bottom, are $\rho_0\sigma_0^3 = 0.3$, 0.2726, 0.3, 0.6, 0.5535, and 0.6 and $\rho_{0'}\sigma_0^3 = 0.6$, 0, 0, 0.3, 0, 0. No matrix-fluid attraction is present. It is clear that templating affects the phase envelope beyond the effect due to available volume.

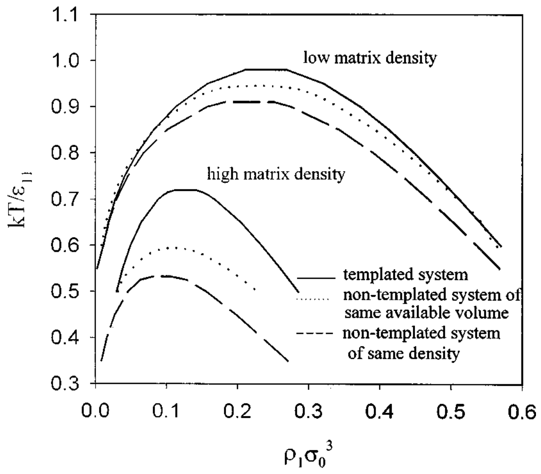

FIG. 2. Liquid-vapor phase envelopes, as described in Fig. 1, with the sole difference that matrix-fluid attraction is equal to fluid-fluid attraction: $\varepsilon_{01} = \varepsilon_{11}$.

$-u_{ij}^P(r)/kT$ for $r \leqslant \sigma_{ij}$, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, σ_i is the hard sphere diameter of component *i*, $u_{ij}^P(r)$ is the perturbation potential between components *i* and *j*, *k* is the Boltzmann constant, and *T* is the absolute temperature. We consider here a truncated Lennard-Jones perturbation potential: $u_{ij}^P(r) = -\varepsilon_{ij}$ for $\sigma_{ij} \leqslant r < 2^{1/6}\sigma_{ij}$, $u_{ij}^P(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$ for $2^{1/6}\sigma_{ij} \leqslant r < 2.5\sigma_{ij}$, and $u_{ij}^P(r) = 0$ for $2.5\sigma_{ij} \leqslant r$. The one remaining closure relation in this approximation is $c_c = c_{11}$ [17]. To account for the fact that the template is removed prior to addition of the fluid phase, we impose the condition that $\sigma_{0'1} = \varepsilon_{0'1} = 0$.

The perturbation contributions to the internal and Helmholtz energies are obtained in the usual way: integration of the product of the pair correlation function times the pair energy and subsequent integration of the Gibbs-Helmholtz equation. The perturbation contributions to the chemical potential and compressibility are determined via first and second derivatives of the free energy with respect to fluid density. The hard sphere reference contribution is determined by integrating the compressibility as in Ref. [19]. Coexisting liquid and vapor densities are calculated using standard techniques to equate liquid and vapor phase chemical potentials and, via the Gibbs-Duhem relation [18], grand potentials.[1]

In Figs. 1 and 2, we show phase envelopes of two matrix densities $\rho_0\sigma_0^3 = 0.3$ and 0.6, for equally sized matrix, template, and fluid diameters $(\sigma_0 = \sigma_0 = \sigma_1)$ with a nonattractive $(\varepsilon_{01} = 0)$ and an attractive $(\varepsilon_{01} = \varepsilon_{11})$ matrix-fluid perturbation interaction. As expected, the critical temperature and the overall two-phase envelope are lowered upon increasing the matrix density. In addition, we observe these properties to increase when the material is formed with a template. This is not unexpected since templating increases the available volume, which in turn is expected to shift the phase diagram upward. The question of whether templating has additional influence on phase behavior is answered by considering a nontemplated matrix of the same available volume as the templated one. Using a diagrammatic theory [12], we find nontemplated model systems of matrix densities $\rho_0\sigma_0^3 = 0.2726$ and 0.5535 to have the same available volumes (respectively) as the two templated systems. For both high and low matrix densities, we find the phase envelopes to lie between those of the templated and nontemplated systems of the same density. This indicates that templating influences the phase diagram beyond what would be expected from the increased available volume. This effect is most pronounced for the higher matrix density, where the critical temperature in a templated system exceeds that of a nontemplated system by about 20%.

To investigate the cause of this template-enhanced phase behavior, we decompose the chemical potential into contributions from hard sphere repulsion and attractive tail perturbation: $\mu_1 = \mu_1^R + \mu_1^P$. We find μ_1^R to increase monotonically and μ_1^P to decrease monotonically with increasing ρ_1. In general, the suppression of phase behavior by the presence of quenched disorder may be explained by an inhibition of the required van der Waals loop: μ_1^P is decreased (in magnitude) by a reduced number of fluid-fluid interactions and μ_1^R is increased by a reduced available volume (to the entire set of fluid particles). In Fig. 3, we show the chemical potential as a function of adsorbed fluid density for templated and nontemplated quenched disorder of the same available volume. The van der Waals loop is much more pronounced in the former. We note that under these conditions it is the templated system that possesses a slightly steeper μ_1^R, so the enhanced van der Waals loop is due solely to a greater (in magnitude) contribution from the attractive perturbation in

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[1] As discussed in Refs. [18, 22], a fluid's mechanical pressure may differ from its thermodynamic pressure (defined as its grand potential density) in quenched matrices. The latter is the appropriate phase coexistence variable.

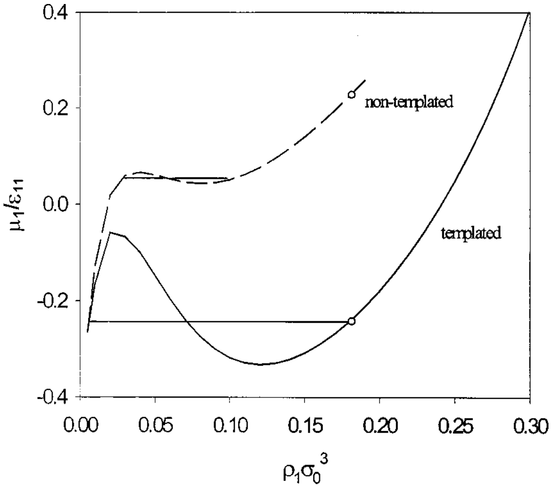

FIG. 3. The chemical potential versus density of a fluid in a system of templated quenched particles ($\rho_0\sigma_0^3 = 0.6$, $\rho_0\sigma_0^3 = 0.3$) and a system of nontemplated quenched particles of the same available volume ($\rho_0\sigma_0^3 = 0.5535$, $\rho_0\sigma_0^3 = 0$) at a temperature of $kT/\varepsilon_{11} = 0.4$. No matrix-fluid attraction is present. The circles represent points where the average numbers of fluid-matrix and fluid-fluid neighbors are calculated (see Table I). The enhanced van der Waals loop of the templated system is due to an increased number of fluid-fluid interactions.

the templated system. This suggests the geometry of the templated matrix to be one that favors fluid-fluid attractive interactions.

To further test this observation, we calculate the average number of neighboring particles [16] as

$$\overline{\langle N_{01}\rangle} = \rho_1 \int_0^{r_{\min}} (h_{01}(r) + 1) d\overline{r}, \tag{8}$$

$$\overline{\langle N_{11}\rangle} = \rho_1 \int_0^{r_{\min}} (h_{11}(r) + 1) d\overline{r}, \tag{9}$$

where $r_{\min}$ is the separation at which the first minimum of the pair correlation function occurs. (The angular brackets and overbar represent averages over fluid and matrix configurations, respectively, as in Ref. [18].) Comparing a coexisting liquid in a templated matrix with a (noncoexisting) liquid at the same temperature and density in a nontemplated matrix of identical available volume, we find the average number of fluid-fluid (fluid-matrix) interactions to be increased (decreased) in the templated system (see Table I). Our conclusion is therefore that fluid-fluid interactions are suppressed to a much lesser degree by templated quenched disorder and that this leads to a more negative μ_1^P and an ‘‘enhanced phase behavior’’ relative to that observed in standard (nontemplated) quenched disorder.

It is unlikely that a considerably simpler approach could yield such a prediction. For example, even a detailed treatment of a hard sphere system, with the attractive perturbation considered within a mean field framework, would be insufficient to explain our result. In that case, μ_1^P would be identical in both matrices and the slightly higher μ_1^R for the fluid in the templated matrix (of the same available volume), as shown in Fig. 5 of Ref. [18], would cause the nontemplated matrix to possess the more pronounced van der Waals loop.

TABLE I. Average number of matrix-fluid (N_{01}) and fluid-fluid (N_{11}) neighbors as determined by Eqs. (8) and (9) for a saturated liquid at $kT/\varepsilon_{11} = 0.4$ (for $\varepsilon_{01} = 0$) and at 0.5 (for $\varepsilon_{01} = \varepsilon_{11}$) in a templated matrix ($\rho_0\sigma_0^3 = 0.6$, $\rho_0\sigma_0^3 = 0.3$) and for a liquid of the same temperature and density in a nontemplated matrix of the same available volume ($\rho_0\sigma_0^3 = 0.5535$, $\rho_0\sigma_0^3 = 0$).

	Templated $\varepsilon_{01} = 0$	Nontemplated $\varepsilon_{01} = 0$	Templated $\varepsilon_{01} = \varepsilon_{11}$	Nontemplated $\varepsilon_{01} = \varepsilon_{11}$
$\overline{\langle N_{01}\rangle}$	2.38	2.75	3.94	4.23
$\overline{\langle N_{11}\rangle}$	5.07	3.97	3.90	3.32

Although only an approximate theory, the mean spherical approximation (MSA) energy approach has been shown to accurately predict the phase behavior of a bulk fluid and a fluid adsorbed in a nontemplated system [14]. We should point out that this approach does not predict a true critical point characterized by a diverging density correlation length; instead, the region near the critical point is described by the usual mean field exponents. We emphasize, however, that only a relatively small region of the phase diagram is affected by this theoretical shortcoming and that an accounting is made for the physical causes of phase transitions away from the critical point, namely, balances between energy and entropy leading to van der Waals loops. In contrast, the MSA compressibility approach fails to predict a phase transformation in the presence of quenched disorder in systems of dimension less than 4 [21].

We take a moment to discuss the nature of the liquid and vapor phases encountered here. Although the density distribution of a fluid in the presence of quenched disorder is inhomogeneous for a given quenched configuration (it becomes homogeneous when averaged over an ensemble of quenched configurations), localized regions of high or low density are not the liquid and vapor phases defined by the phase envelopes. Points on (or outside) the envelopes are true thermodynamic phases immersed in the quenched disorder. Implicitly, the interface between coexisting phases is neglected, its influence vanishing in the thermodynamic limit. In this sense, a Kelvin equation [23] or Gibbs-Thomson relation [24] analysis, which considers the effect of interfacial shape on the equilibrium between a localized region and a bulk phase, is not directly useful for predicting the true phase envelope. Furthermore, a Kelvin-equation-based approach predicts an altered pressure of coexistence but not an altered critical temperature; this is incompatible with observations made here and elsewhere [13–16]. Finally, because of the high density and small particle size of the quenched disorder considered here, it would be difficult to assign a geometry to an interface separating regions of higher and lower fluid density. However, for quenched disorder consisting of particles much larger than those of the imbibed fluid, this difficulty may be lessened and the Kelvin equation could provide useful information on the effect of local condensation on the overall isotherm.

We thank Pascal Viot, Julian Talbot, Gilles Tarjus, and Eduardo Glandt for helpful discussions and the National Science Foundation (Grant No. CTS-9876599) and the American Chemical Society's Petroleum Research Fund (Grant No. 34163-G9) for financial support.

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[1] *Spin Glass and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1997).
[2] M. C. Goh, W. I. Goldburg, and C. Knobler, Phys. Rev. Lett. **58**, 1008 (1987).
[3] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **58**, 1865 (1987); P. Wiltzius, S. B. Dierker and B. S. Dennis, *ibid.* **62**, 804 (1989); S. B. Dierker and P. Wiltzius, *ibid.* **66**, 1185 (1991).
[4] A. P. Y. Wong and M. H. W. Chan, Phys. Rev. Lett. **65**, 2567 (1990); A. P. Y. Wong, S. B. Kim, W. I. Goldburg, and M. H. W. Chan, *ibid.* **70**, 954 (1993).
[5] B. J. Frisken, F. Ferri, and D. S. Canell, Phys. Rev. Lett. **66**, 2754 (1991); B. J. Frisken and D. S. Canell, *ibid.* **69**, 632 (1992); B. J. Frisken, F. Ferri, and D. S. Canell, Phys. Rev. E **51**, 5922 (1995).
[6] T. Michalski, A. Benini, and G. H. Findenegg, Langmuir **7**, 185 (1991); M. Thommes and G. H. Findenegg, *ibid.* **10**, 4270 (1994); M. Thommes, G. H. Findenegg, and M. Schoen, *ibid.* **11**, 2137 (1995).
[7] M. Y. Lin, S. K. Sinha, G. M. Drake, X. I. Wu, P. Thiyagarajan, and H. B. Stanley, Phys. Rev. Lett. **72**, 2207 (1994).
[8] W. D. Machin, Langmuir **10**, 1235 (1994); **15**, 169 (1999).
[9] K. Morishige and M. Shikimi, J. Chem. Phys. **108**, 7821 (1998).
[10] F. Brochard and P. G. de Gennes, J. Phys. (France) Lett. **44**, L785 (1983), P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984).
[11] N. K. Raman, M. T. Anderson, and C. J. Brinker, Chem. Mater. **8**, 1682 (1996).
[12] P. R. Van Tassel, Phys. Rev. E **60**, R25 (1999).
[13] K. S. Page and P. A. Monson, Phys. Rev. E **54**, R29 (1996).
[14] M. Alvarez, D. Levesque, and J.-J. Weis, Phys. Rev. E **60**, 5495 (1999).
[15] D. M. Ford and E. D. Glandt, Phys. Rev. E **50**, 1280 (1994).
[16] E. Kierlick, M. L. Rosinberg, G. Tarjus, and P. Monson, J. Chem. Phys. **106**, 264 (1997).
[17] J. A. Given, Phys. Rev. A **45**, 816 (1992); J. A. Given and G. Stell, J. Chem. Phys. **97**, 4573 (1992).
[18] M. L. Rosinberg, G. Tarjus, and G. Stell, J. Chem. Phys. **100**, 5172 (1994).
[19] L. Zhang and P. R. Van Tassel, J. Chem. Phys. **112**, 3006 (2000); L. Zhang and P. R. Van Tassel, Mol. Phys. **98**, 1521 (2000).
[20] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1986).
[21] E. Pitard, M. L. Rosinberg, G. Stell, and G. Tarjus, Phys. Rev. Lett. **74**, 4361 (1995).
[22] E. Kierlick, M. L. Rosinberg, G. Tarjus, and P. Monson, J. Chem. Phys. **103**, 4256 (1995).
[23] H. T. Davis, *Statistical Mechanics of Phases, Interfaces, and Thin Films* (VCH, New York, 1996).
[24] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996).