PHYSICAL REVIEW E VOLUME 57, NUMBER 4 APRIL 1998

Liquid polymorphism of simple fluids within a van der Waals theory

Carlos F. Tejero[1] and Marc Baus[2]
[1]*Facultad de Ciencias Físicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain*
[2]*Faculté des Sciences, Case Postale 231, Université Libre de Bruxelles, B-1050 Brussels, Belgium*

(Received 2 October 1997)

We show how a van der Waals theory of simple fluids with an interaction potential whose range has a nonmonotonic density dependence can lead to a liquid-liquid transition in close analogy to recent observations and simulations. [S1063-651X(98)00104-4]

PACS number(s): 61.20.Ne, 64.70.Ja, 64.10.+h, 05.70.Ce

Increasing evidence is being found that some pure substances can exhibit a liquid-liquid transition in the metastable (supercooled) region [1,2]. Such a higher degree of polymorphism of the disordered phase [3], while common for mixtures [4], is unexpected for a simple fluid. Indeed, while the rules of thermodynamics do not exclude the possibility of there being more than two different fluid phases in a simple fluid, the common experience is to find at most two: a low-density fluid (or vapor) phase and a high-density fluid (or liquid) phase. The presence of a thermodynamically stable liquid in the phase diagram of a simple fluid is moreover not a universal feature since its presence is known to strongly depend on the range of the interparticle potential. It is only when the range of the attractions is sufficiently long compared to the range of the repulsions that the liquid becomes a thermodynamically stable phase [5]. This whole scenario is already well described by the simple van der Waals (vdW) theory of [6]. Here we show moreover that the same vdW theory also predicts the possible existence of a second fluid-fluid transition in addition to the usual vapor-liquid transition whenever the range of the attractions exhibits a nonmonotonic density dependence. It is found, however, that, even for long-ranged attractions, this liquid-liquid transition can still be thermodynamically metastable relative to the fluid-solid transition, in agreement with the expectations of [1,2].

The vdW theory, although very simple, embodies a qualitatively correct description of the vapor-liquid transition and, when suitably extended to the solid phase [6], also of the complete phase diagram of a pure substance or ''simple fluid.'' The Helmholtz free energy per particle at the number density ρ and temperature T, $f(\rho,T)$, can be written as

$$f(\rho,T)=f_{\rm id}(\rho,T)-Ts(\rho,T)+e(\rho,T), \tag{1}$$

where $f_{\rm id}(\rho,T)=k_BT[\ln(\rho\Lambda^3)-1]$ is the ideal gas contribution (k_B being Boltzmann's constant and Λ the thermal de Broglie wavelength), $s(\rho,T)$ the excess (over ideal) entropy per particle, and $e(\rho,T)$ the excess energy per particle. The first basic assumption of the vdW theory is to ascribe $s(\rho,T)$ entirely to the repulsions that when represented by a hard-sphere potential lead to the well-known ''covolume'' expression $s(\rho)=k_B\ln(1-b\rho)$ for the excess entropy of the fluid phase. Note that this implies that the fluid phase is mechanically stable only up to the maximum density $\rho_0=1/b$, b being a constant (here we have used $\rho_0=0.495/v_0$, where v_0 is the hard-sphere volume, a value that, as discussed in detail in [6], leads to a reasonable hard-sphere transition). The second basic assumption of the vdW theory ascribes likewise $e(\rho,T)$ entirely to the attractions that, in the mean-field approximation, yield then the well-known ''cohesion energy'' expression $e(\rho)=\frac{1}{2}\rho\int d\mathbf{r}\; V_A(r)$ for the excess energy of a fluid phase for which the attractions are described by the pair potential $V_A(r)$. For the systems considered in [1,2] the interaction potential has *anisotropic* features and we propose, in a first approximation, to replace it by an average or effective *isotropic* potential [7]. Such an effective potential, resulting, for instance, from preaveraging the anisotropic potential over the angular degrees of freedom with a density-dependent angular correlation function, will generally be density dependent, viz., $V_A(r;\rho)$ [8], and the above expression of the cohesion energy of the fluid phase will thus be replaced by

$$e(\rho)=\frac{1}{2}\rho\int d\mathbf{r}V_A(r;\rho)\equiv\rho E(\rho), \tag{2}$$

where $E(\rho)$ contains now all the supplementary density dependence introduced by $V_A(r;\rho)$. The fact that $E(\rho)$ is no longer a constant can eventually have a profound influence on the phase diagram. For instance, the equations that determine the critical point of the fluid phase become now

$$2a(\rho_c)-(\rho_0-\rho_c)a'(\rho_c)=0,$$
$$\rho_0^2k_BT_c=(\rho_0-\rho_c)^2a(\rho_c), \tag{3}$$

where T_c is the critical temperature, ρ_c is the critical density, $\rho_0=1/b$, the prime indicates a derivative with respect to the argument, and $a(\rho)\equiv-\rho[2e'(\rho)+\rho e''(\rho)]$. When $E(\rho)$ is a constant, $e(\rho)$ and $a(\rho)$ are linear in ρ, in which case Eq. (3) has only one solution, the standard vdW vapor-liquid critical point [namely, $\rho_c=\rho_0/3$, $k_BT_c=-8e(\rho_0)/27$]. When $E(\rho)$ is not a constant, Eq. (3) can eventually have more than one (physical) solution leading hereby to liquid polymorphism of a degree higher than 2 (each additional critical point introducing an additional liquid phase). Since little is known about $E(\rho)$ itself, we work backward and focus directly on Eq. (3) and $a(\rho)$. In the spirit of a simple virial correction we tentatively write $a(\rho)=-2\rho(1-\alpha\rho)^2E(0)$, where α is a positive constant so as to enforce a nonmonotonic behavior and the square is necessary in order to

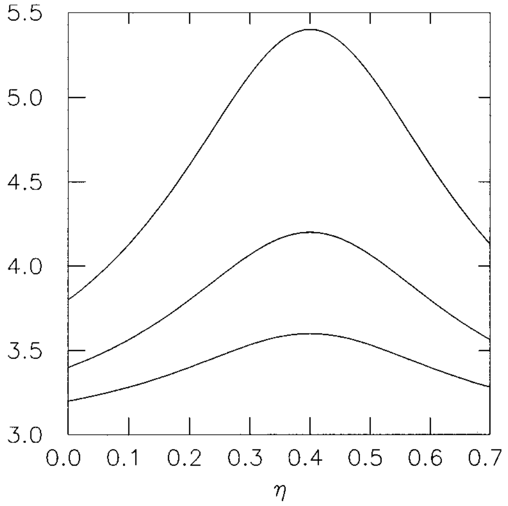

FIG. 1. Density dependence of the index $n \equiv n(\rho)$ of the inverse power potential of Eq. (5) as obtained from Eq. (6) with $\alpha = 5v_0$ versus the reduced density $\eta = \rho v_0$, with $v_0 = \pi\sigma^3/6$ and σ being the hard-sphere diameter. The three cases shown correspond to (from top to bottom) $n(0) = 3.8$, 3.4, and 3.2. Note the pronounced maximum in $n(\rho)$ for the larger $n(0)$ values.

keep T_c of Eq. (3) positive [note that for attractions $E(\rho) < 0$]. Integrating the relation between $E(\rho)$ and $a(\rho)$ yields then

$$E(\rho) = \left(1 - \frac{2}{3}\alpha\rho + \frac{1}{6}\alpha^2\rho^2\right)E(0), \tag{4}$$

which when substituted into Eq. (3) leads to two critical points (there also is a spurious third solution corresponding to $T_c = 0$). Note that $E(\rho)$ has a maximum of $E(0)/3$ at $\alpha\rho = 2$. This nonmonotonic variation of $E(\rho)$ reflects a nonmonotonic variation of the potential parameters. Indeed, assuming for simplicity an inverse power potential

$$V_A(r;\rho) = \begin{cases} 0 & (r < \sigma) \\ -\epsilon\left(\dfrac{\sigma}{r}\right)^{n(\rho)} & (r \geqslant \sigma), \end{cases} \tag{5}$$

where ϵ is an amplitude fixing the temperature scale and σ the hard-sphere diameter fixing the density scale, Eqs. (2) and (5) yield $E(\rho) = -\epsilon 2\pi\sigma^3/[n(\rho) - 3]$ and Eq. (4) implies

$$n(\rho) = 3 + \frac{n(0) - 3}{1 - \dfrac{2}{3}\alpha\rho + \dfrac{1}{6}\alpha^2\rho^2}, \tag{6}$$

i.e., a potential index $n(\rho)$ that rises from its zero-density value $n(0)$ to a maximum value $3[n(0) - 2]$ and then decreases to $n(\rho_0)$ (see Fig. 1). This rise of $n(\rho)$ with ρ has a *destabilizing* effect on the liquid, which splits the liquid-vapor transition into two succesive transitions, each of which ends in a separate critical point. In order to keep the physical parameters of these critical points positive, the value of α has to be kept within some ‘‘physical’’ range. For illustrative purposes we have chosen here $\alpha = 5v_0$.

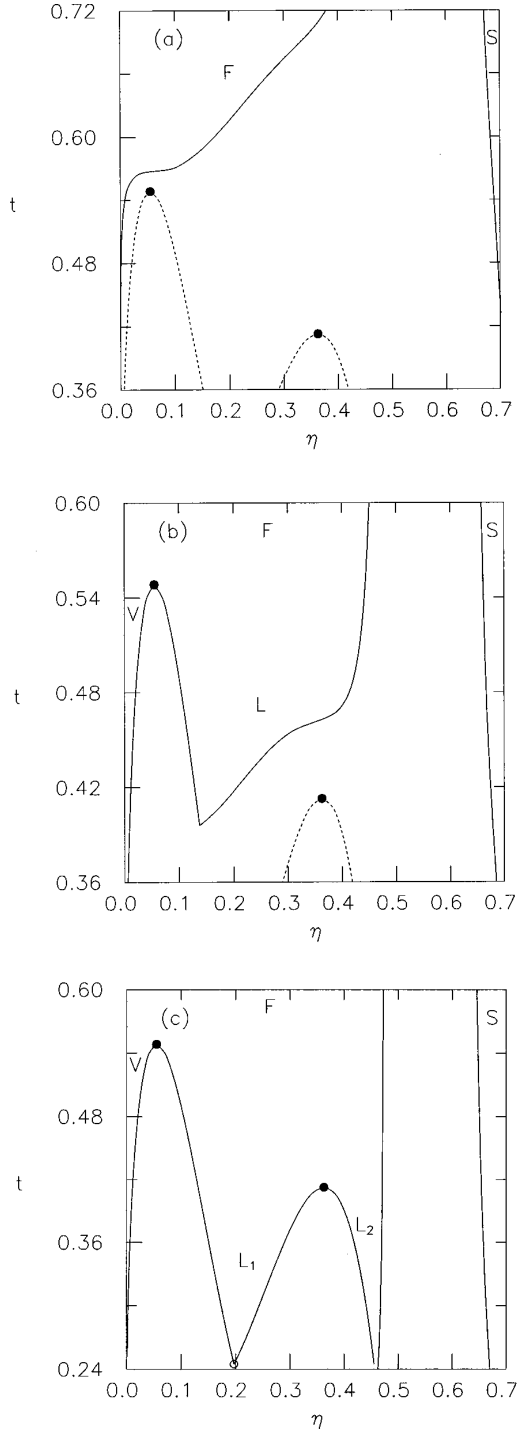

FIG. 2. Complete phase diagram (F for fluid, V for vapor, L for liquid, and S for solid) of a simple fluid in the temperature-density plane (t,η), with $t = [n(0) - 3]k_BT/\epsilon$ and $\eta = \rho v_0$, for a system with an effective potential given by Eqs. (5) and (6) with $\alpha = 5v_0$, as obtained from the present vdW theory. The three cases shown correspond to (a) $n(0) = 3.8$, (b) $n(0) = 3.4$, and (c) $n(0) = 3.2$. The thermodynamically stable coexistencies are drawn as full lines, the metastable coexistencies as dotted lines, the critical points by full dots, and the vapor-liquid-liquid triple line passes through the open dot. The number of stable critical points of (a), (b), and (c) is, respectively, zero, one and two. Note the upward ‘‘push’’ in the liquid-solid coexistence curve of (a) and (b) due to the proximity of the metastable liquid-liquid critical point.

As is well known, the appearance of loops in the free energy $f(\rho,T)$ of the fluid phase is not a sufficient condition for finding fluid-fluid transitions in the system's phase diagram. The ultimate thermodynamic stability of these transitions still depends crucially on the relative position of the fluid and solid free energies or, more precisely, on the convex envelope to these free energies. To assess the thermodynamic stability of the liquid polymorphism induced by Eq. (6) it is thus essential to consider also the solid phases and the fluid-solid transitions. This can be done by extending the above considerations to the solid phase along the lines put forth in [6]. To this end the excess entropy of Eq. (1) can be evaluated for the solid phase within a cell-theory approximation as $s(\rho)=3k_B \ln[1-(\rho/\rho_{\mathrm{CP}})^{1/3}]$, where ρ_{CP} is the density at close packing of the crystal structure considered [here a face-centered-cubic (fcc) structure], while the excess energy of Eq. (1) will be approximated for the solid (see [6] for details) by the lattice energy $e(\rho)=\frac{1}{2}\Sigma_j V_A(r_j;\rho)$, where r_j is the distance of site j to a site placed at the origin. For the inverse power potential of Eq. (5) this lattice sum can be written as $e(\rho)=-\epsilon\alpha_M(n)(\rho/\rho_{\mathrm{CP}})^{n/3}$, where $\alpha_M(n)$ is the fcc Madelung constant for an inverse power potential of index n, with here $n=n(\rho)$ as given by Eq. (6). The relative stability of the fluid-fluid, solid-solid, and fluid-solid transitions is then seen to be controlled by the only remaining free parameter $n(0)$, which determines the range of the zero-density potential $V_A(r;\rho=0)$. The crucial role of the range of the interaction potential in modern liquid state theory was already emphasized in [5,6]. For instance, in the case where $n(\rho)$ is a constant, viz., $n(\rho)=n(0)$, the above theory indicates that the liquid phase is thermodynamically stable only for $3<n(0)<7.6$, while under these circumstances any isostructural solid-solid transition is always metastable (see [6] for details). Here, because of the pronounced maximum in $n(\rho)$ shown in Fig. 1, the liquid will be metastable unless the maximum value of $n(\rho)$, namely, $3[n(0)-2]$, satisfies $3<3[n(0)-2]<7.6$. Even so we find (the situation depends still on the value chosen for α, but the present scenario has been found for $4.09<\alpha/v_0<5.29$) that for $n(0)=3.8$ the two (vapor-liquid and liquid-liquid) critical points are still metastable with respect to the fluid-solid transition. With a further decrease of $n(0)$ the low-density (vapor-liquid) critical point becomes stable while for very low values of $n(0)$ the high-density (liquid-liquid) critical point also can eventually become stable, introducing then a vapor-liquid-liquid triple point. For the intermediate $n(0)$ values $[n(0)\simeq 3.5]$ the phase diagram obtained here (see Fig. 2) exhibits a striking similarity to that of [1]. Notice also that the proximity of the metastable liquid-liquid critical point can be observed indirectly as producing a bump in the liquid-solid coexistence curve (see Fig. 2).

In conclusion, we have shown how liquid polymorphism follows from a simple vdW theory for a pure substance (simple fluid) with a long-ranged pair potential whose range exhibits a nonmonotonic density variation. The similarity of the resulting phase behavior to that put forth in [1,2] is striking, although the liquid polymorphism of the systems considered in [1,2] could of course have a different physical origin. In particular, the route to liquid polymorphism put forth here is purely energetic, while entropic considerations can clearly lead to a similar result, as could an interplay between both mechanisms.

M.B. acknowledges financial support from the Fonds National de la Recherche Scientifique (Belgium) and C.F.T. that from the Dirección General de Investigación Científica y Técnica (Spain), Grant No. PB94-0265.

---

[1] P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, Science **275**, 322 (1997).

[2] See, e.g., S. Harrington, R. Zhang, P. H. Poole, F. Sciortino, and H. E. Stanley, Phys. Rev. Lett. **78**, 2409 (1997); C. J. Roberts, A. Z. Panagiotopoulos, and P. G. Debenedetti, *ibid.* **77**, 4386 (1996); K. H. Smith, E. Shero, A. Chizmeshya, and G. H. Wolf, J. Chem. Phys. **102**, 6851 (1995); P. H. Poole, F. Sciortino, T. Grande, H. E. Stanley, and C. A. Angell, Phys. Rev. Lett. **73**, 1632 (1994); H. E. Stanley, C. A. Angell, U. Essmann, M. Hemmati, P. H. Poole, and F. Sciortino, Physica A **205**, 122 (1994); P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).

[3] Also referred to as ''polyamorphism'' in the case of glass phases. See, for example, C. J. Roberts and P. G. Debenedetti, J. Chem. Phys. **105**, 658 (1996); C. A. Angell, P. H. Poole, and J. Shao, Nuovo Cimento D **16**, 993 (1994).

[4] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth, London, 1982).

[5] A. P. Gast, C. K. Hall, and W. B. Russel, J. Colloid Interface Sci. **96**, 251 (1983); E. J. Meijer and D. Frenkel, J. Chem. Phys. **100**, 6873 (1994); C. F. Tejero, A. Daanoun, H. N. W. Lekkerkerker, and M. Baus, Phys. Rev. Lett. **73**, 752 (1994); S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E **51**, 1344 (1995); C. Rascón, G. Navascués, and L. Mederos, Phys. Rev. B **51**, 14899 (1995).

[6] A. Daanoun, C. F. Tejero, and M. Baus, Phys. Rev. E **50**, 2913 (1994); T. Coussaert and M. Baus, *ibid.* **52**, 862 (1995); M. Baus, T. Coussaert, and R. Achrayah, Physica A **232**, 575 (1996); M. Baus and R. Achrayah, J. Phys.: Condens. Matter **8**, 9633 (1996).

[7] See, e.g., R. O. Watts and I. J. Mc Gee, *Liquid State Chemical Physics* (Wiley-Interscience, New York, 1976).

[8] In the present treatment we have neglected any temperature dependence of the effective potential. This may be the reason why the coefficient of thermal expansion remains positive in this simplified model.