

Simple fluids with complex phase behavior

Gianpietro Malescio and Giuseppe Pellicane

Dipartimento di Fisica, Università di Messina and Istituto Nazionale Fisica della Materia, 98166 Messina, Italy

(Received 26 May 2000; published 22 January 2001)

We find that a system of particles interacting through a simple isotropic potential with a softened core is able to exhibit a rich phase behavior including: a liquid-liquid transition in the supercooled phase, as has been suggested for water, a gas-liquid-liquid triple point, a freezing line with anomalous reentrant behavior. The essential ingredient leading to these features resides in the presence of two effective radii in the repulsive core. The potential investigated appears appropriate for a class of spherical polymeric micelles recently investigated.

DOI: 10.1103/PhysRevE.63.020501

PACS number(s): 61.20.Gy, 61.25.Hq, 64.70.-p

Predicting the phase behavior for a given interparticle interaction is a central problem in statistical physics. The issue is relatively well assessed for pure systems interacting through a variety of radially symmetric pair potentials, such as hard-spheres, Lennard-Jones systems, inverse-power potentials, etc. The complexity of the phase diagram increases for pure substances characterized by complex interactions depending on the intermolecular orientation, e.g., water, C,S,Ga, Se,Te,I₂,Cs,SiO₂, etc. [1]. For the above materials somewhat exotic features appear in the phase diagram, such as fluid-fluid or liquid-liquid transitions, polyamorphism, and multiple crystalline structures. Exploring the possibility that simple fluids interacting through suitable *isotropic* potentials may exhibit similar behaviors represents a major challenge. The importance of such model systems is not limited to providing a better understanding of the components of the interaction responsible for the above phase behaviors. They may also represent an adequate description for systems having a completely different nature: the suspensions of colloidal particles dispersed in a fluid medium. In fact, in these systems, through the experimental control of particle and solvent properties [2], it is possible to generate “nonstandard” effective pair interactions similar to those investigated in this Rapid Communication.

Such features of the phase diagram as fluid-fluid transitions, polyamorphism, etc. may be related to the competition between expanded and compact structures. This suggests that the potential should possess two equilibrium positions [3]. The most obvious form with such a feature is one with two wells. Such potentials were shown to give rise to waterlike thermodynamic anomalies, though the presence of a new critical point could not be directly observed [4]. Another form of interparticle interaction which could produce different equilibrium positions is that in which there is a region of negative curvature in the repulsive core: these so-called softened-core potentials were proposed by Hemmer and Stell [5] who argued that they might produce an additional transition, if a first already exists. Recently, through a mixed numerical–mean field type calculation, it was found that a potential consisting of a softened-core plus an infinite range van der Waals attractive term may give rise to a second critical point [6]. Very recently, molecular dynamics simulation showed for a softened-core potential with an attractive well evidence of a transition between two fluid phases in the supercooled region [7].

The purpose of this article is to report the findings of a study of the phase behavior of a system of particles interacting through a potential with a softened-core and an attractive well. Our analysis, based mainly on thermodynamically self-consistent (TSC) integral equations for fluids [8] and partly on Monte Carlo (MC) simulations, shows the existence of a liquid-gas critical point in the stable fluid phase and of a liquid-liquid critical point in the supercooled region. The liquid-gas and liquid-liquid coexistence lines meet in a gas-liquid-liquid triple point. Moreover, the behavior of the freezing line, estimated through one-phase criteria [9–11], such as the Hansen-Verlet (HV) rule [10] and the entropic criterion based on the analysis of residual multiparticle entropy [11], is consistent with the existence of multiple crystalline structures in the solid phase. Unlike previous studies [12,13], we show that a microscopic theory, directly linking the behavior of the system to the form of the interparticle pair potential, predicts for a simple fluid the existence of a liquid-liquid critical point and of a gas-liquid-liquid triple point.

The chosen potential has a repulsive part $V_{rep}(r)$ consisting of a hard core of radius $r_0 = \sigma$ and a repulsive square shoulder of height ϵ and radius $r_1 = 2.5\sigma$, plus an attractive component $V_{attr}(r)$ having the form of a square well of depth 1.25ϵ extending from $r_1 = 2.5\sigma$ to $r_2 = 3\sigma$ [13]. To reach a thorough comprehension of the role played by the different components of the potential we first study its purely repulsive part, and then consider the effect of adding the attractive component.

Let us consider a system of particles interacting through the potential $V_{rep}(r)$. We study its structural and thermodynamical properties using the TSC Roger-Young (RY) integral equation [14]. Figure 1 illustrates the structure factor $S(k)$ for different densities, at a constant temperature, as calculated within the above theory and through MC simulations [15,16]. We note the unusual behavior of the first peaks of $S(k)$ which, as the density increases, progressively rise and fall (with the exception of the third peak, which grows monotonously with the density). This anomalous structure factor recalls in its essential features that which is observed in dense star polymer solutions [16]. The “rising and falling” of the peaks of $S(k)$ reflects the turning on and off, upon the density increasing, of different effective length scales. When T and ρ are sufficiently small, the soft core is practically impenetrable and the particles behave as hard

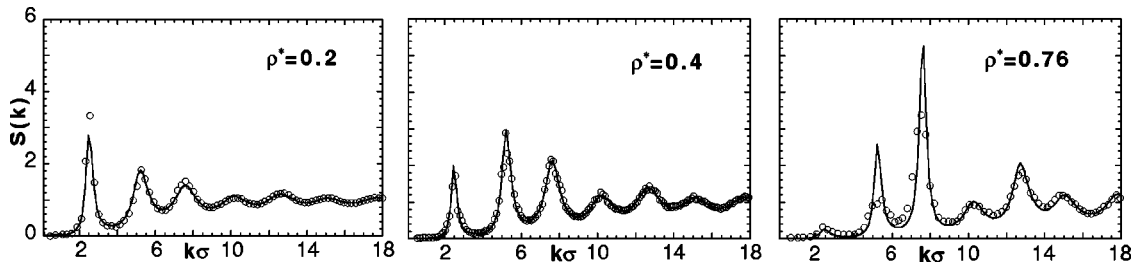


FIG. 1. Purely repulsive potential. Structure factors within the RY equation (solid line) and MC simulation (circles) at a reduced temperature $T^* = k_B T / \epsilon = 0.285$ and at different values of the reduced density $\rho^* = \rho \sigma^3$.

spheres of radius r_1 . As T and ρ increase, more and more particles penetrate the soft core until this becomes scarcely influent and the system is essentially equivalent to an assembly of hard spheres of radius r_0 . In general, the system can be considered a ‘‘mixture’’ of two populations of hard spheres, of radius r_0 and r_1 respectively. The relative concentration of the two species is fixed by the values of T and ρ . Thus, in contrast to standard simple fluids, the system has three possible length scales: r_1 , $r_{10} = (r_1 + r_0)/2$ and r_0 , and as many indicators of structural ordering, namely, the peaks of the structure factor corresponding to the wave vectors k_1 , k_{10} , and k_0 , associated with these lengths.

According to the HV rule a fluid is expected to undergo crystallization when the first (main) peak of $S(k)$ attains the value 2.85 [10]. This statement usually refers to simple fluids with a single length scale, so its extension to the ‘‘anomalous’’ simple fluid investigated is not straightforward. Since in our case different length scales come into play, one has to consider all the associated indicators of structural ordering. In Fig. 2 we show the loci of the points of the plane T, ρ for which $S(k_1)$, $S(k_{10})$, and $S(k_0)$ are equal to 2.85. The freezing line predicted by the HV rule coincides with the line which bounds the region where at least one of the peaks of $S(k)$ is greater than 2.85. This line shows a reentrant behavior (at intermediate densities) which can be related to the peculiar penetrability of the softened-core. In fact, the frac-

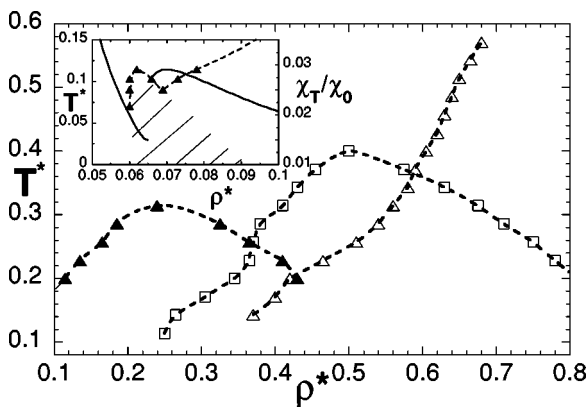


FIG. 2. Purely repulsive potential. The dashed lines are the loci of points of the T, ρ plane where $S(k_1)$ (closed triangles), $S(k_{10})$ (squares), and $S(k_0)$ (open triangles) are equal to 2.85. The inset shows a magnification of the low T -low ρ region; the isothermal compressibility χ_T (thick solid line) is calculated along the isotherm $T^* = 0.103$ (χ_0 is the ideal gas compressibility).

tion of particles penetrating the soft core increases with the density (at constant T), thus ‘‘generating’’ additional space for the system. This effect is particularly important where one length scale begins to become less effective in favor of the smaller one. In these regions the phenomenon may overcompensate the general decrease, upon the density increasing, of the space available to the particles, thus causing a tendency of the system to become less ordered; accordingly, the freezing line may have a negative derivative, i.e., the system may undergo crystallization upon the density *decreasing*. To this regard we note that reentrant freezing and melting transitions originated by an ultrasoft repulsive pair potential have been observed, through MC calculations, in star polymers solutions [17]; in the same work the validity of HV rule for such systems was confirmed.

A reentrant behavior of the freezing line is also observed in the low T -low ρ region shown in the inset in Fig. 2. Here, the freezing line starts nearly vertical at $\rho^* \approx 0.06$, which corresponds to the freezing density $\rho r_1^3 \approx 0.943$ of a fluid of hard spheres of radius r_1 . As ρ increases, the freezing line bends and exhibits a negative derivative. The phenomenon can be associated with the very onset of the soft core penetration which, for the reasons discussed above, has a disordering effect on the system. Consequently, the system undergoes melting with volume contraction, as confirmed by the fact that, in correspondence of the portion of the freezing line having negative derivative, (i) the isothermal compressibility exhibits an anomalous behavior suddenly increasing with the density (see the inset in Fig. 2) and (ii) the first peak of $S(k)$, which corresponds to the effective length scale r_1 , undergoes a strongly localized decrease (see Fig. 3). These features also occur along the extension of the freezing line towards lower temperatures, suggesting, in this case, the transition to a less ordered solid phase. The extrapolation of this line meets the $T=0$ axis at $\rho^* \approx 0.09$, which corresponds to the closest packing of hard spheres of radius r_1 (occurring at $\rho r_1^3 = \sqrt{2}$). The above results lead us to conclude that the region shadowed in the inset of Fig. 2 corresponds to an *expanded* solid phase of the system.

We now investigate the phase behavior of a system of particles interacting through the full potential $V_{rep}(r)$ plus $V_{attr}(r)$. Calculations are performed making use of the HMSA TSC equation [a suitable combination of the hypernetted chain (HNC) equation and of the soft-mean spherical approximation (SMSA) equation, proposed in Ref. [18]], which is better suited than the RY equation for interparticle

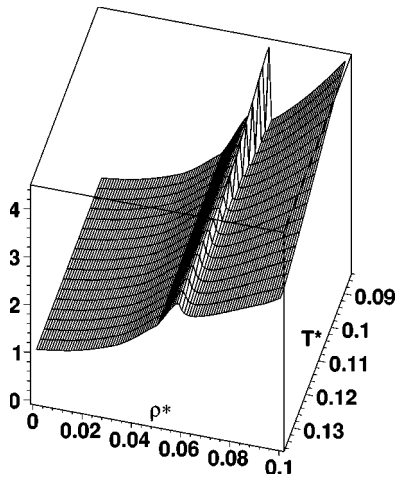


FIG. 3. Purely repulsive potential. Three-dimensional plot of $S(k_1)$ as a function of T^* and ρ^* .

interactions including an attractive component and reduces to this for purely repulsive potentials. The phase diagram of the system is shown in Fig. 4. Two coexistence curves occur [19], each terminating at a critical point, denoted $C1$ and $C2$. The critical densities and temperatures are respectively $\rho_{C1}^* = 0.06$, $T_{C1}^* = 1.3$, and $\rho_{C2}^* = 0.77$, $T_{C2}^* = 0.55$. These values were estimated using the rectilinear diameter rule and the scaling relationship for the width of the coexistence curve with the nonclassical exponent $\beta \approx 0.325$ [20]. Below T_{C1} the system separates into a gas and a liquid phase. The liquid phase is not unique since, below T_{C2} ($T_{C2} < T_{C1}$), separates into distinct low-density (LD) and high-density (HD) phases. We stress that this phenomenon is crucially related to the softened-core form of the potential. Due to the presence of the penetrable repulsive shoulder particles can be in one of two “states”: this is the essential feature which opens the possibility of liquid-liquid-immiscibility in a pure substance.

Since the critical point $C2$ is well below the freezing line, the liquid-liquid transition occurs between metastable phases in the supercooled region of the system. This feature recalls the scenario proposed for water [3], but in that case the liquid-liquid coexistence line is expected to start from the $C2$ point running at higher pressures as T decreases [21]. In the system investigated, the contrary is observed, this line running at lower pressures as T decreases (see inset of Fig. 4). This makes a new feature possible: the simultaneous coexistence of three fluid phases. In fact, the gas-liquid and the liquid-liquid coexistence lines meet in a gas-liquid-liquid triple (GLL) point which lays in the supercooled phase ($\rho_{GLL}^* \approx 0.57$, $T_{GLL}^* \approx 0.53$). In order to check that the metastable states close to the critical point $C2$ have a finite lifetime, we performed MC runs consisting of not less than 5×10^8 steps, finding no evidence of structural ordering (which suggests that point $C2$ lays above the melting line of the system). The MC and theoretical radial distribution functions are in overall good agreement with each other [22]. In principle, one cannot exclude that at such temperatures and

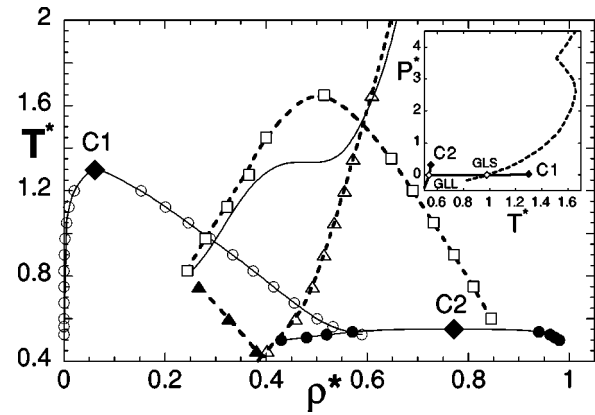


FIG. 4. Phase diagram in the (T, ρ) plane. Coexistence lines: gas-liquid (solid line with open circles), liquid-liquid (solid line with closed circles). The closed diamonds represent the critical points. The dashed lines are the loci of points where $S(k_1)$ (closed triangles), $S(k_{10})$ (squares), and $S(k_0)$ (open triangles) are equal to 2.85. The solid line with no symbols is the freezing line estimated through the entropic criterion. Inset: P, T phase diagram showing the freezing line estimated within HV rule (dashed line), the liquid-gas coexistence line (solid line ending in $C1$) and the liquid-liquid coexistence line (solid line ending in $C2$); the open diamonds represent the triple points; pressure is given in units of ϵ/σ^3 .

densities the system might undergo a glass transition. In this case, our results would be consistent with the existence of LD and HD amorphous phases [3].

The addition of the attractive well causes a shift towards higher temperatures of the loci of the points where $S(k_1)$, $S(k_{10})$, and $S(k_0)$ are equal to 2.85, while their location in density remains essentially unaltered. Only a small portion of the line $S(k_1) = 2.85$ is visible since it lays almost entirely in a region, corresponding approximately to the gas-liquid spinodal decomposition, where the theory is unstable. At intermediate densities the freezing line predicted by the HV rule shows a very evident reentrant behavior. As shown in the inset in Fig. 4, the freezing temperature increases initially with pressure, then decreases in the pressure range $2.5 \leq P^* \leq 3.5$ ($P^* = P\sigma^3/\epsilon$), and eventually increases again. We further note that the freezing line meets the liquid-gas coexistence line in a gas-liquid-solid (GLS) triple point ($\rho_{GLS}^* \approx 0.29$, $T_{GLS}^* \approx 0.97$). For comparison we also show, in Fig. 4, the freezing line estimated through the entropic criterion. This is in reasonable agreement with HV rule though there is a discrepancy in the intermediate region: the reentrant behavior predicted by the entropic criterion is, in fact, scarcely evident and can be appreciated only numerically [22]. Though our estimate of the freezing line is based solely on one-phase criteria, its shape, with branches having distinctly different slopes, is consistent with the possibility that structural changes occur in the solid state of the system. Consequently, transitions may be possible between solid phases of the system investigated.

The results presented in this article show that a pure model system, interacting through an isotropic potential with two characteristic radii in the repulsive core, may have a rich

phase behavior with features typical of substances characterized by much more complex anisotropic interactions. On the other hand, the above potential could be appropriate for a class of spherical macromolecules. Experimental results [23] show, in fact, that it is possible to realize polymeric micelles for which the ratio of the diffuse corona thickness to the dense core radius is close to that of the repulsive shoulder-hard core radii in our model system. Additional features of

the interaction may be fixed through appropriate tuning of particle and solvent properties.

We wish to thank P. Ballone, C. Caccamo, S. Dugdale, P.V. Giaquinta, and F. Mallamace for useful and interesting discussions. One of us (G.M.) expresses his gratitude to H.E. Stanley for stimulating his interest in the subject. G.M. would like to thank MURST PRIN 2000 for financial support. G.P. would like to thank INFN for financial support.

-
- [1] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1998); V.V. Brazhkin *et al.*, High Press. Res. **6**, 363 (1992); Phys. Lett. A **154**, 413 (1991); M.C. Bellisent-Funel, Europhys. Lett. **42**, 161 (1998).
- [2] P.N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J.P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991); *The Physics of Complex Fluids*, edited by F. Mallamace and H.E. Stanley (IOS Press, Amsterdam, 1997).
- [3] O. Mishima and H.E. Stanley, Nature (London) **396**, 329 (1998); **392**, 164 (1998).
- [4] M.R. Sadr-Lahijany *et al.*, Phys. Rev. Lett. **81**, 4895 (1998).
- [5] P.C. Hemmer and G. Stell, Phys. Rev. Lett. **24**, 1284 (1970); G. Stell and P.C. Hemmer, J. Chem. Phys. **56**, 4274 (1972).
- [6] E.A. Jagla, J. Chem. Phys. **111**, 8980 (1999).
- [7] G. Franzese *et al.*, e-print cond-mat/0005184.
- [8] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, New York, 1986).
- [9] Motivations for the use of one-phase criteria come from the difficulty to perform free energy calculations. In fact, due to the softened core, there are many possible solid phases and in general it is not easy to safely tell which is the most stable structure [10], except in the limit case of a very narrow shoulder, which can be treated perturbatively [11].
- [10] E.A. Jagla, J. Chem. Phys. **110**, 451 (1999).
- [11] P. Bolhuis and D. Frenkel, J. Phys.: Condens. Matter **9**, 381 (1997).
- [12] Phase diagrams with a second critical point were derived within studies based on extensions of the van der Waals theory [13].
- [13] C.F. Tejero and M. Baus, Phys. Rev. E **57**, 4821 (1998); P.H. Poole *et al.*, Phys. Rev. Lett. **73**, 1632 (1994).
- [14] F.J. Rogers and D.A. Young, Phys. Rev. A **30**, 999 (1984).
- [15] MC calculations were performed using a standard Metropolis algorithm [16] within the *NVT* ensemble for a system of 1000 particles. The thermodynamic state of interest was reached by annealing the system, starting from an FCC lattice configuration at high temperature. We monitored the initial “melting” of the lattice by checking the zeroing of the translational order parameter. The equilibration cycles were extended well beyond the point in which the instantaneous values of the potential energy and pressure cease to show a systematic drift and begin to oscillate about steady mean values. For each thermodynamic state equilibration cycles consist of at least 2×10^8 MC steps for all the particles (with acceptance rate between 0.3 and 0.4). The structure factor is calculated through cumulation runs of $2 \times 10^7 - 10^8$ MC steps (depending on the density) through the relationship $S(k) = \langle \rho(k) \rho(-k) \rangle$. Test runs with 5000 particles were performed to check for finite size effects.
- [16] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, London, 1987).
- [17] M. Watzlawek, C.N. Likos, and H. Löwen, Phys. Rev. Lett. **82**, 5289 (1999).
- [18] G. Zerah and J.P. Hansen, J. Chem. Phys. **84**, 2336 (1986).
- [19] The coexistence curves are calculated by equating, at constant T and P , the chemical potentials of the coexisting phases. Generally, TSC integral equations are derived assuming that local consistency is equivalent to global consistency [18]. Since in the low T -high ρ region this approximation is not very satisfactory and global consistency is unpracticable, the pressure is calculated along mixed isochore-isothermal paths which minimize the isochore portions where the more accurate “compressibility route” pressure cannot be evaluated.
- [20] J.M. Yeomans, *Statistical Mechanics of Phase Transitions* (Clarendon Press, Oxford, 1992).
- [21] P.H. Poole, F. Sciortino, U. Essmann, and H.E. Stanley, Nature (London) **360**, 324 (1992).
- [22] G. Pellicane and G. Malescio (unpublished).
- [23] G.A. McConnell *et al.*, Phys. Rev. Lett. **71**, 2102 (1993); G.A. McConnell and A.P. Gast, Macromolecules **30**, 435 (1997).