Fluid-fluid or liquid-liquid transitions have been proposed for many different substances such as supercooled water, C,S,Ga,Se,Te,I2, Cs,SiO2 etc. The transition may occur between stable phases as in carbon or between metastable phases as has been suggested in supercooled water. In general, these substances also exhibit different amorphous states as well as multiple crystalline structures. The complex intermolecular interactions characterizing the above materials are usually modeled through anisotropic potentials depending on the molecular orientation and thus the possibility that simple fluids interacting through isotropic potentials may exhibit similar exotic phase behaviors is a challenging field of investigation.

As argued by Mishima and Stanley the competition between expanded and compact structures in fluid-fluid (liquid-liquid) transitions suggests that the potential should possess two equilibrium positions. The most obvious form with such feature is one with two wells. Such potentials were shown to give rise to water-like thermodynamic anomalies, though the presence of a new critical point could not be directly observed. 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 Stell and Hemmer who argued that they might produce a second 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. Very recently, molecular dynamics simulation showed for a softened-core potential with an attractive square well evidences of a transition between two fluid phases in the supercooled region.

The purpose of this Letter is to report the findings of a study of the phase behavior of a system of particles interacting through a potential consisting of a hard core with a finite repulsive shoulder and an attractive square well. Our analysis, based mainly on thermodynamically self-consistent (TSC) integral equations for fluids 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 such as the Hansen-Verlet (HV) rule and the entropic criterion based on the analysis of residual multiparticle entropy, is consistent with the existence of multiple crystalline structures in the solid phase. This is the first time that a microscopic theory 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 \( V_{\text{rep}}(r) \) consisting of a hard core of radius \( r_0 = \sigma \) and a repulsive square shoulder of height \( \epsilon \) and radius \( r_1 = 2.5\sigma \), plus an attractive component \( V_{\text{attr}}(r) \) having the form of a square well of depth \( 1.25\epsilon \) extending from \( r_1 = 2.5\sigma \) to \( r_2 = 3\sigma \). 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.

As a preliminary investigation we study through MC simulation a system of particles interacting through the potential \( V_{\text{rep}}(r) \) in 2D, since in this case the spatial arrangement of the particles can be easily visualized. Snapshots representing the configuration of the system at a low temperature and different densities are shown in Fig.1, together with the corresponding structure factors \( S(k) \). As the density increases, the system rapidly undergoes a very strong ordering (Fig.1(b)) indicated by the huge first peak of \( S(k) \) (the splitted second peak of \( S(k) \) can be related to the presence of lattice dislocations evident in the figure). Upon further increasing the density, particles begin to enter the soft core and many hard cores get in contact: the first peak of \( S(k) \) decreases while the second peak of \( S(k) \) is considerably enhanced (Fig.1(d)). Finally at very high densities (not shown in the figure) the third peak of \( S(k) \) becomes the highest one, while the first two peaks are greatly depressed.
The progressive “rising and falling” of the peaks of the structure factors reflects the turning on/off of different effective length scales. When the temperature $T$ and the density $\rho$ are sufficiently small, the soft core is practically impenetrable and the particles behave as hard spheres of radius $r_1$. As $T$ and $\rho$ 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 $\rho$. 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 wavevectors $k_1$, $k_{10}$, $k_0$, associated to these lengths. We stress the crucial role of these regions the phenomenon may overcompensate the behavior which suggests that the system may undergo behavior which is expected to be reliable. The freezing line starts nearly vertical at a density $\rho^* \approx 0.06$ which corresponds to the freezing density $\rho r_1^3 \approx 0.945$ of a fluid of hard spheres of radius $r_1$. As $\rho$ increases, the freezing line bends and shows a reentrant behavior: the phenomenon is associated with the very onset of the soft core penetration which, for the reasons above discussed, has a disordering effect on the system. This is reflected in the anomalous behavior shown by the isothermal compressibility $\chi_T$, which suddenly increases with the density (see same figure). Correspondingly, the first peak of $S(k)$ abruptly decreases: this occurs also at lower temperatures (where the value of $S(k_1)$ remains however greater than 2.85) along a line coinciding approximately with the extension of the portion of the freezing line with negative derivative. This line meets the $T = 0$ axis at a density $\rho^* \approx 0.09$ 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 to conclude that the region shadowed in the inset of Fig.3 corresponds to an expanded solid phase of the system.

We now investigate the phase behavior of a system of particles interacting through the potential $V_{\text{rep}}(r)$ in 3D. We study its structural and thermodynamical properties using the TSC Roger-Young (RY) integral equation \[23\]. According to 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 refers to simple fluids with a single length scale. In our case, different length scales come into play and one must consider all the associated indicators of structural ordering. As shown in Fig.2, their behavior, upon increasing the density at constant $T$, appears analogous to that observed in 2D, with each peak in turn rising and then “falling” down (except that associated to the hard core radius which becomes higher and higher as $\rho$ increases). The overall trend is confirmed by MC calculation, though the theory \[24\] tends to overestimate the heights of $S(k_{10})$ and $S(k_0)$ at high densities.

In Fig.3 we show the locii of the points of the plane $T, \rho$ for which $S(k_1)$, $S(k_{10})$ and $S(k_0)$ are equal to 2.85. The freezing line predicted through a straightforward application of HV rule to the “anomalous” simple fluid investigated, should coincide with the line which bounds the region where at least one of the peaks of the structure factor is greater than 2.85. This line shows a reentrant behavior which suggests that the system may undergo crystallization upon the density decreasing. The behavior can be related to the presence of the finite repulsive shoulder. In fact, the fraction 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 of the space available to the system upon the density increasing thus causing a tendency of the system to become less ordered: accordingly, the freezing line may have a negative derivative. We note, however, that this behavior might be overestimated in Fig.3. In fact, since different length scales are contemporarily effective and contribute to the global structural ordering of the system, we expect that a more realistic freezing line has a smoother behavior which “blends” together the upper portions of the different curves of Fig.3.

The inset in Fig.3 shows a magnification of the low temperature-low density region. Here, since only one length scale ($r_1$) is effective, the prediction of $HV$ is expected to be reliable. The freezing line starts nearly vertical at a density $\rho^* \approx 0.06$ which corresponds to the freezing density $\rho r_1^3 \approx 0.945$ of a fluid of hard spheres of radius $r_1$. As $\rho$ increases, the freezing line bends and shows a reentrant behavior: the phenomenon is associated with the very onset of the soft core penetration which, for the reasons above discussed, has a disordering effect on the system. This is reflected in the anomalous behavior shown by the isothermal compressibility $\chi_T$, which suddenly increases with the density (see same figure). Correspondingly, the first peak of $S(k)$ abruptly decreases: this occurs also at lower temperatures (where the value of $S(k_1)$ remains however greater than 2.85) along a line coinciding approximately with the extension of the portion of the freezing line with negative derivative. This line meets the $T = 0$ axis at a density $\rho^* \approx 0.09$ 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 to conclude that the region shadowed in the inset of Fig.3 corresponds to an expanded solid phase of the system.

We now investigate the phase behavior of a system of particles interacting through the potential $V_{\text{rep}}(r)$ plus $V_{\text{attr}}(r)$. Calculations are performed making use of the HMSA TSC equation \[23\] which is better suited than RY equation for interparticle 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 \[23\], 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 non-classical exponent $\beta \approx 0.325 \[29\]$. 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. 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 \[19\], but in that case the liquid-liquid coexistence line is expected to start
from C2 running at higher pressures as $T$ decreases. In the system investigated, the contrary is observed, this line running at lower pressures as $T$ decreases (see inset of Fig.4). This makes possible a new feature: the simultaneous coexistence of three fluid phases. In fact, the gas-liquid and the liquid-liquid coexistence lines meet in the supercooled phase ($\rho_{GLL}^* \approx 0.57$, $T_{GLL}^* \approx 0.53$).

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, correspondingly approximately to the gas-liquid spinodal decomposition, where the theory is unstable. The freezing line corresponding to HV rule and that estimated through the entropic criterion are in substantial agreement at low and high densities (pressures), yielding close estimates of the gas-liquid-solid (GLS) triple point ($\rho_{GLS}^* \approx 0.29$, $T_{GLS}^* \approx 0.97$). On the contrary, these lines differ markedly in the intermediate region, where the first one shows a very evident reentrant behavior, while in the second approach this can be appreciated only numerically. For the reasons exposed in the purely repulsive case, the second result is probably more reliable. Thus, as shown in the inset in Fig.4, the freezing temperature increases initially with pressure, then remains essentially constant (according to the entropic criterion) in the pressure range $1 \leq P^* \leq 2$, ($P^* = P\sigma^3/\epsilon$) and eventually increases again with pressure. 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 Letter show that a pure model system, with a softened-core isotropic potential, may have a rich phase behavior with features typical of substances characterized by much more complex anisotropic interactions. The possibility that simple substances related to the model investigated may exist (or may be “realized”) in nature well deserves to be investigated.

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FIG. 1. 2D system. Snapshots showing the configurations calculated through MC simulation at a reduced temperature $T^* = k_B T / \epsilon = 0.05$ ($k_B$ is the Boltzmann constant) and different reduced densities $\rho^* = \rho \sigma^D$ ($D$ is the dimensionality of the system and $\rho$ is the number density of the particles). Below each snapshot the corresponding structure factor is shown. Dots represent the hard core of the particles.

FIG. 2. Purely repulsive potential. Structure factors within the RY equation and MC simulation.
FIG. 3. Purely repulsive potential. The dashed lines are the locii of points of the $T,\rho$ plane where $S(k_1)$ (full triangles), $S(k_0)$ (squares) and $S(k_0)$ (open triangles) are equal to 2.85. The inset shows a magnification of the low $T$-low $\rho$ region; the isothermal compressibility $\chi_T$ (thick solid line) is calculated along the isotherm $T^* = 0.103$ ($\chi_0$ is the ideal gas compressibility).
FIG. 4. Phase diagram in the $T,\rho$ plane. Coexistence lines: gas-liquid (circles), liquid-liquid (dots). The full diamonds represent the critical points. The dashed lines are the locii of points where $S(k_1)$ (full 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; pressure is given in units of $\epsilon/\sigma^3$. 
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