PHYSICAL REVIEW E **74**, 041201 (2006)

Generalized van der Waals theory of liquid-liquid phase transitions

Yu. D. Fomin, V. N. Ryzhov, and E. E. Tareyeva
Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142190, Moscow Region, Russia

(Received 27 February 2006; revised manuscript received 29 June 2006; published 3 October 2006)

In the framework of the thermodynamic perturbation theory for fluids we study how the phase diagram of an isotropic repulsive soft-core attractive potential, where a liquid-liquid phase transition exists in addition to the standard gas-liquid phase transition, changes by varying the parameters of the potential. We show that there are some regions in a potential parameter space where a high-density liquid-liquid critical point can exist in addition to the conventional gas-liquid critical point. It is also found that there is a correlation between the behavior of the phase diagram as a function of width of the repulsive step and the structure of the correlation function of a reference liquid.

DOI: 10.1103/PhysRevE.74.041201 PACS number(s): 61.20.Gy, 61.20.Ne, 64.60.Kw

I. INTRODUCTION

Despite the growing interest to the possible polymorphic phase transitions in liquids and glasses [1,2], the nature of different phases which can be found in dense (and possibly metastable) liquids is still puzzling. The coexistence of different phases, while common for mixtures, is unexpected for a simple fluid. In principle, the rules of thermodynamics do not forbid the existence of more than two different fluid phases in a simple fluid, however, from a common experience only two of them are well known: low density fluid (vapor) and high-density fluid (liquid) phases. At the same time in recent years experimental evidences of such features of the phase diagram as liqiud-liquid transitions, polyamorphism, etc., appeared for a wide range of systems including water, Si, I, Se, S, P, etc. [1–15]. The complexity of the phase diagrams in these substances may be a result of complex interactions depending on the intermolecular orientations.

At the same time exploring the possibility that simple fluids interacting through isotropic potentials may exhibit similar behavior represents a serious challenge for theorists.

It was shown recently through molecular dynamics simulations that a system of particles with the isotropic repulsive soft-core attractive potential may have high-density and low-density liquid phases [17,18] (see also [19–21]). This potential may be considered as an effective potential resulting from an average over the angular degrees of freedom for systems where the position of the minimum approach between particles depends on their relative orientations such as in the case of the hydrogen bonding between water molecules [1,5,13,22]. This potential also may be used to model interactions in a variety of systems including liquid metals, colloids, silica [1,22–26].

After the pioneering work by Hemmer and Stell [16], where the soft-core potential with an attractive interaction at large distances was first proposed for the qualitative explanation of the isostructural phase transitions in materials such as Ce or Cs, a lot of attention was paid to the investigation of the properties of the systems with the potentials that have a region of negative curvature in their repulsive core.

In spite of the simplicity of the model, the physical mechanism that causes the liquid-liquid phase transition in such systems is not completely understood. As was emphasized in Refs. [27,28], it arises from an interplay of the different components of the pair interaction. In Refs. [27,28] the authors tried to disentangle the role of each component to investigate the dependence of the phase diagram on the potential parameters. In Ref. [27] the results of molecular dynamic calculations performed for several sets of parameters were presented. The resulting behavior of the critical points was interpreted through a modified van der Waals equation where the effect of the repulsive shoulder at different densities ρ and temperatures T can be taken into account by an effective excluded volume depending on both ρ and T. In Ref. [28] the same analysis was undertaken by using an integral equation approach in the hypernetted-chain approximation. In Refs. [27,28] it was shown that the high-density liquid-liquid critical point can be found only when there is some kind of balance between the attractive and repulsive parts of the potential.

It should be noted that it is widely believed (see, for example, Refs. [29,30]) that a fluid-fluid transition should be related to the attractive part of the potential. However, in Refs. [31,32] in the framework of the generalized van der Waals theory it was shown that the purely repulsive step potential is sufficient to explain the high-density liquid-liquid phase transition.

II. PHASE DIAGRAMS

In the present paper we apply the generalized van der Waals theory to the study of the phase diagram of the system of particles interacting through an isotropic potential with an attractive well and a repulsive component consisting of a hard core plus a finite shoulder. This potential can be written in the form

$$\Phi(r)=\begin{cases}\infty, & r\le d,\\ \varepsilon, & d<r\le\sigma,\\ -\varepsilon_1, & \sigma<r\le\sigma_1,\\ 0, & r>\sigma_1.\end{cases} \tag{1}$$

The potential is shown in the inset in Fig. 1. We apply to the problem the first order thermodynamic perturbation theory for fluids. The soft-core plus the attractive well of the potential (1) are treated as perturbation with respect to the

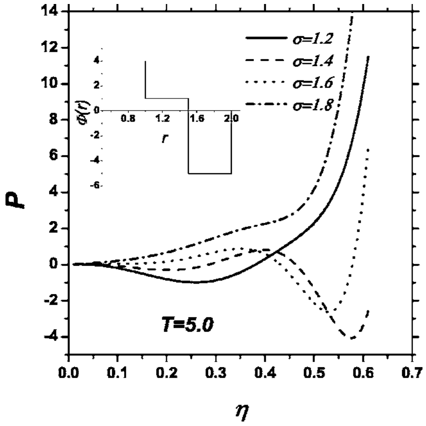

FIG. 1. The pressure isotherms for the system with the potential shown in the inset for $\varepsilon/\varepsilon_1=5$ and for different values of σ/d for $T=5$ ($\sigma_1/d=2$). Inset: An isotropic potential with an attractive well and a repulsive component consisting of a hard core plus a finite shoulder.

hard sphere potential. In this case the free energy of the system may be written in the form [33,34]

$$\frac{F-F_{HS}}{Nk_BT}=\frac{1}{2}\rho\beta\int u_1(r)g_{HS}(r)d\mathbf{r}, \qquad (2)$$

where $\rho=N/V$ is the mean number density, $\beta=1/k_BT$, $u_1(r)$ is the perturbation part of the potential $u_1(r)=\Phi(r)-\Phi_{HS}(r)$, $\Phi_{HS}(r)$ is the hard sphere singular potential, and $g_{HS}(r)$ is the hard sphere radial distribution function which is taken in the Percus-Yevick approximation [35].

To calculate F_{HS}, one can use, for example, the approximate equation [34]

$$\frac{F_{HS}}{k_BTN}=3\ln\lambda-1+\ln\rho+\frac{4\eta-3\eta^2}{(1-\eta)^2}. \qquad (3)$$

Here $\lambda=h/(2\pi mk_BT)^{1/2}$ and $\eta=\pi\rho\sigma^3/6$.

The conventional van der Waals theory is obtained after the further assumption that the molecules are randomly distributed, i.e., $g_{HS}(r)=1$ for $r>d$ [34,36]. This approximation corresponds to the structureless reference liquid. In this case after substitution of Eq. (1) in the right-hand side of Eq. (2) one has

$$\frac{F-F_{HS}}{Nk_BT}=-a\rho, \qquad (4)$$

where

$$a=\frac{2\pi\beta}{3}[\varepsilon_1(\sigma_1^3-\sigma^3)-\varepsilon(\sigma^3-d^3)]. \qquad (5)$$

As is well known, a conventional van der Waals equation is obtained from Eq. (4) using thermodynamic relation $P=\rho^2(\frac{\partial F}{\partial\rho})_T$. If $a<0$, in the system there are no phase transitions; if $a>0$, there is only a gas-liquid phase transition. So in the framework of the conventional van der Waals theory it is impossible to describe an additional liquid-liquid phase transition, and one has to take into account a density dependence of the radial distribution function of the reference liquid. As will be seen further, in this case the interplay between the structure of the reference liquid and the form of the potential has an essential influence on the phase diagram of the system. For these reasons we call the approach presented in this article by "generalized van der Waals theory."

Further in this paper we use the dimensionless quantities $\tilde{\mathbf{r}}=\mathbf{r}/d$, $\tilde{P}=Pd^3/\varepsilon$, $\tilde{V}=V/Nd^3=1/\tilde{\rho}$, $\tilde{T}=k_BT/\varepsilon$, omitting the tilde marks. We also use a packing fraction $\eta=\frac{\pi\rho d^3}{6}=\frac{\pi\tilde{\rho}}{6}$.

The results of the calculations are demonstrated in Figs. 1–5. In Fig. 1 a typical family of pressure isotherms is shown for the system with $\varepsilon_1/\varepsilon=5$ for different values of σ/d for $T=5$. The van der Waals loops in the isotherms at low temperatures are clearly seen, this indicates the existence of the first order liquid-gas and liquid-liquid phase transitions for some sets of the potential parameters.

In order to investigate the dependence of the phase diagrams on the parameters of the potential (1) we consider two cases. In the former case the overall length of the potential is fixed: $\sigma_1/d=3.0$. The latter case corresponds to the constant width of the attractive well $(\sigma_1-\sigma)/d=0.5$ and variable σ.

In Fig. 2 the evolution of the phase diagram is shown as a function of σ/d for the fixed value of $\sigma_1/d=3$. The dashed lines correspond to spinodals which as usual are calculated from the condition $\partial P/\partial\rho=0$ and the solid lines are the equilibrium lines of gas-liquid and liquid-liquid phase transitions calculated by using the Maxwell construction (binodals). One can see that for small values of σ there is only gas-liquid transition with very high critical temperature due to large width of the attractive well. If the value of σ/d increases the second (liquid-liquid) transition develops, the critical temperature being lower than for the pure gas-liquid transition. When the difference $\sigma_1/d-\sigma/d$ is small enough (≈ 0.2), the gas-liquid transition disappears, and one has the only high-density fluid-fluid transition, as was discussed in Refs. [31,32]. This transition may be called a liquid-liquid phase transition because it takes place between two high-density fluid phases (high-density liquid and low-density liquid). It should be noted that in this case $a=-10.334$ [see Eq. (5)], so in the framework of the conventional van der Waals approach there is no phase transition. In this case the potential is close to the pure repulsive step potential. As was shown in Refs. [31,32] in the framework of the generalized van der Waals theory, the liquid-liquid phase transition does exist in this system. It should be noted that this scenario is in agreement with the results of Refs. [27,28].

We cannot extend the transition lines down to zero temperature and make calculations for $\sigma_1/d<1.3$ because of the limitation of the perturbation approach.

Before we study the second case, let us consider the system with a purely repulsive step potential, which corresponds to the case $\sigma=\sigma_1$ in Eq. (1). Figure 3 shows the families of the pressure isotherms for different values of σ/d. One can see some kind of periodic behavior as a function of the repulsive step radius σ which apparently correlates with the behavior of the radial distribution function $g_{HS}(r)$. One can see that for small values of σ there is no phase transition. The fluid-fluid phase transition appears in the vicinity of $\sigma/d\approx 1.5$ and disappears again for $\sigma\approx 2.0$. Upon further increase of σ the isotherms reveal some tendencies to forma-

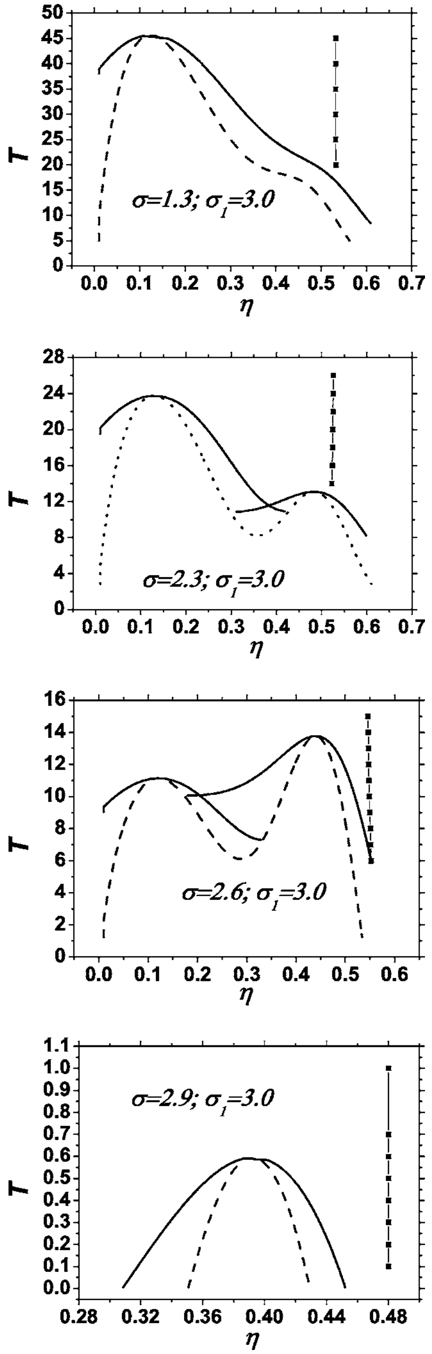

FIG. 2. Phase diagram of the system of particles interacting through the potential (1) for different values of σ/d and the fixed value of $\sigma_1/d=3$. Solid lines correspond to binodals and the dashed lines to spinodals. Squares represent the approximate locations of the fluid-solid transition obtained by equating the free energies of the fluid and solid.

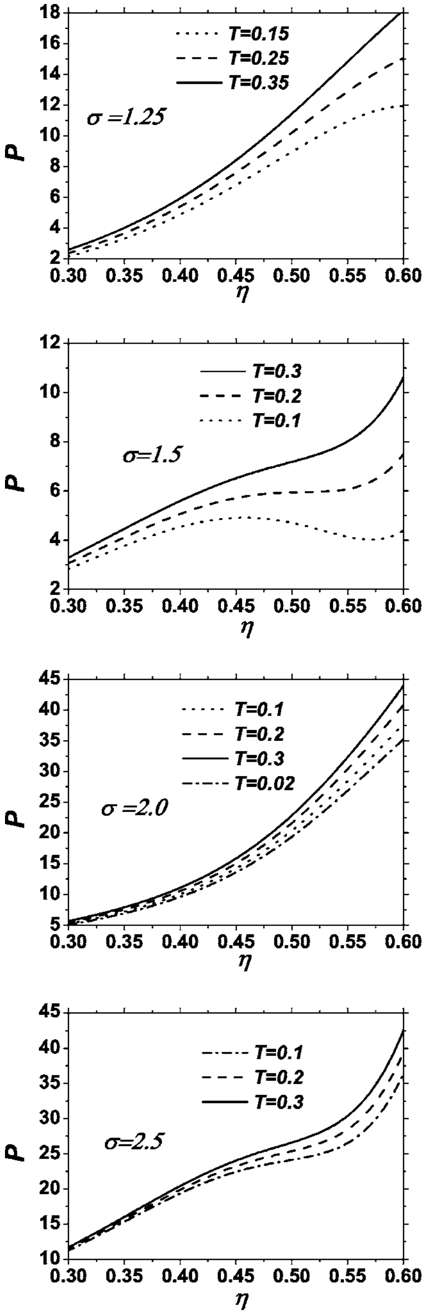

FIG. 3. The families of pressure isotherm for the purely repulsive step potential [$\sigma=\sigma_1$ in Eq. (1)] for different values of σ.

tion of the van der Waals loops. This behavior may be understood from the right-hand side of Eq. (2). One can see that $r\approx1.5$, $r\approx2.0$, and $r\approx2.5$ approximately correspond to the first minimum, second maximum, and second minimum of the radial distribution function $g_{HS}(r)$. As it is seen from Eq. (2), for $\sigma\approx1.5$ the contribution to the free energy of the system comes from the first coordination sphere, which changes most drastically under the fluid-fluid phase transition. A similar situation takes place for $\sigma\approx2.5$, where the contribution corresponds to the first and second coordination shells. For $\sigma\approx2.0$ the contribution is more smooth and, it seems, cannot lead to the transition.

The scenario depicted above strongly correlates with the case when the attractive well is added to the potential. Figure 4 shows the evolution of the phase diagram of the system of particles interacting through the potential (1) for different values of σ/d and fixed value of the difference $\Delta\sigma=\sigma_1/d-\sigma/d=0.5$. Phase diagrams in Fig. 4 demonstrate similar "periodic" behavior as a function of the repulsive step radius σ as one can see in Fig. 4. It should be noted that the attractive well not only leads to the gas-liquid phase tran-

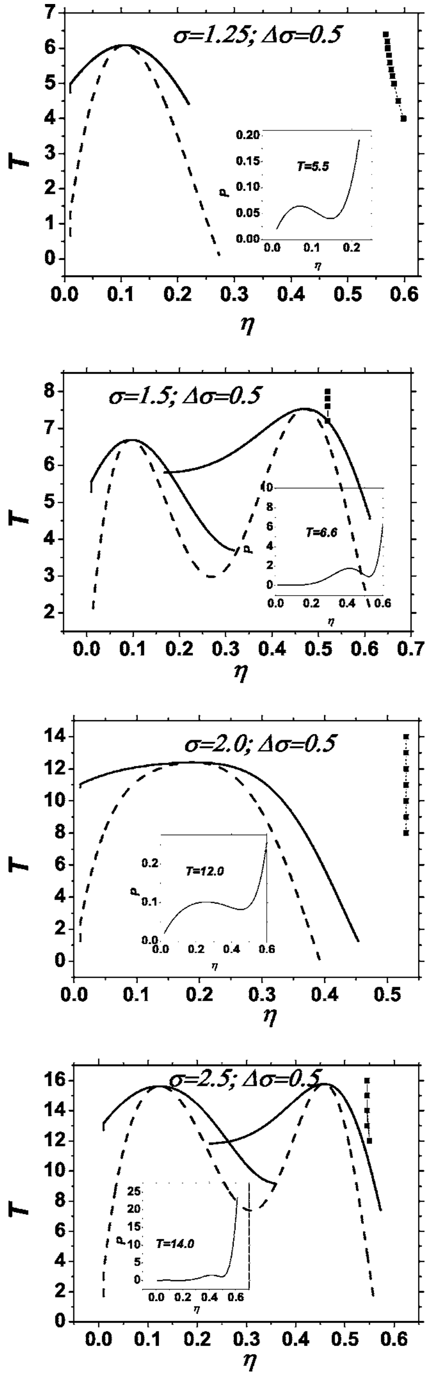

FIG. 4. Phase diagram of the system of particles interacting through the potential (1) for different values of σ/d and fixed value of $\Delta\sigma=\sigma_1/d-\sigma/d=0.5$. Solid lines correspond to binodals and the dashed lines to spinodals. Insets show the characteristic isotherms. Squares represent the approximate locations of the fluid-solid transition obtained by equating the free energies of fluid and solid.

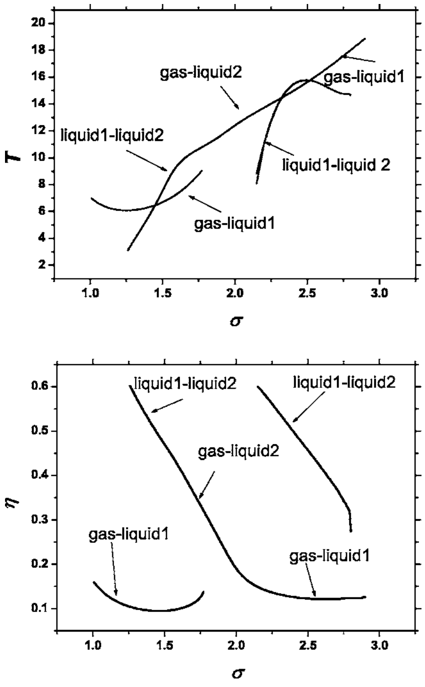

FIG. 5. Dependence of the critical temperatures T (upper figure) and the densities η (lower figure) on the parameter σ for fixed $\Delta\sigma=0.5$

sition but also considerably stabilizes the liquid-liquid phase transition. From Fig. 4 one can see that the critical temperature of the liquid-liquid phase transition in the presence of the attractive well is much higher than the critical temperature of the fluid-fluid phase transition in the underlying purely repulsive step potential system. Moreover, for $\sigma/d=2.5$ there is only tendency to the transition in the system with the repulsive step potential (Fig. 4), however, in the presence of the attractive well one finds the well-defined liquid-liquid phase transition (Fig. 4).

Complex phase behavior shown in Fig. 4 is summarized in Fig. 5 where the dependence of the critical temperatures and densities on the parameter σ for fixed $\Delta\sigma=0.5$ is represented. The most interesting feature is the discontinuity in the appearance of the second transition, which is clearly seen from the lower part of Fig. 5. One can see that the second transition disappears at $\sigma\approx1.75$ and reappears only at $\sigma\approx2.15$. As was discussed above, this behavior is obviously related to the positions of the maxima of a reference radial distribution function (or the structure of the reference liquid). One can see that the second transition is absorbed by the first one when the radius of the repulsive step and correspondingly the position of the attractive part of the potential approximately coincides with the positions of the first and second maxima of the radial function $g_{HS}(r)$. (See also Fig. 2 in Ref. [38] for the similar behavior of the melting line of the two-dimensional system with *attractive* well potential.)

In Figs. 2 and 4 we also show rough estimations of locations of high-density branches of solid-liquid transition (squares). These lines were obtained by equating the fluid free energy [Eq. (2)] and the solid free energy calculated in the framework of the first order perturbation theory for solids [39–42]. For larger values of σ, one can expect that the liquid-liquid phase transition may occur in the stable fluid region. The complete phase diagram, including liquid-solid phase transition, will be presented in a separate publication.

III. SOFT MODEL POTENTIAL

To illustrate the application of the generalized van der Waals theory to other systems let us consider the potential which has the form

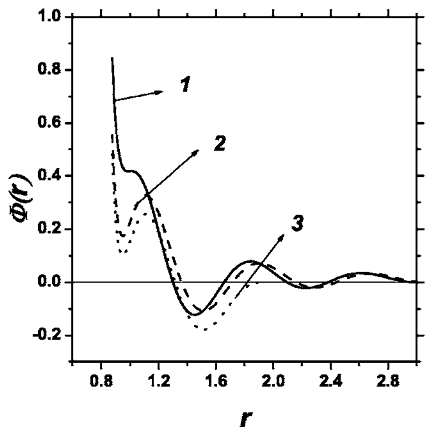

FIG. 6. The potential (6) for $r_0=1.1$ (line 1) and $r_0=1.16$ (line 2). Line 3 is obtained from line 2 by the shift downward by the height of the first maximum.

$$\Phi(r) = \frac{a\exp(-\alpha r)\cos[2k_F(r-r_0)]}{r^3} + b\left(\frac{\sigma}{r}\right)^{18} + \Phi_c, \quad (6)$$

for $r < r_c$ and 0 otherwise. Here r_c is a a cutoff distance. We consider three types of potentials (see Fig. 6). In cases 1 and 2 we use the position of the third minimum of the function (6) as the cutoff distance, in case three, the position of the second maximum. Φ_c is defined through the equation $\Phi(r_c)=0$, i.e., Φ_c shifts the potential so that it vanishes at the cutoff distance making the function and its first derivative continuous at r_c. This potential is a modification of the potential considered in Ref. [43]. The physical meaning of the potential is the following: the first term has a form similar to that expected for the effective interaction between metal ions when screened by electrons. Freidel oscillations are present with wave vector $2k_F$, where k_F corresponds to the wave vector at the Fermi level. The second term adds a repulsive interaction that suppresses the oscillations at small r. The potential looks similar to the effective pair potentials often derived for the metallic systems [23–26], however in the latter case the potentials are density dependent. This means that the present model cannot be used for the calculations of properties of liquid metals directly, however, the most important feature of the potential (6), a repulsive shoulder (or negative curvature of the potential), may be found in the effective potentials of some metals [23–26] and, in principle, can lead to anomalous behavior of liquid metals, including possible liquid-liquid phase transition.

In Fig. 6 this potential is shown for the parameters $\alpha=0.1$, $a=0.5$, $k_F=4.1$, $\sigma=0.331$, $b=0.42\times 10^8$, $r_0=1.1$ (line 1), and $r_0=1.16$ (line 2). Line 3 is obtained from line 2 by the shift downward by the height of the second maximum.

In Fig. 7 the corresponding families of isotherms are shown for different temperatures. To calculate the equation of state corresponding to the potential (6) we apply the thermodynamic perturbation theory. The second part of the potential (6) was considered as a reference system,

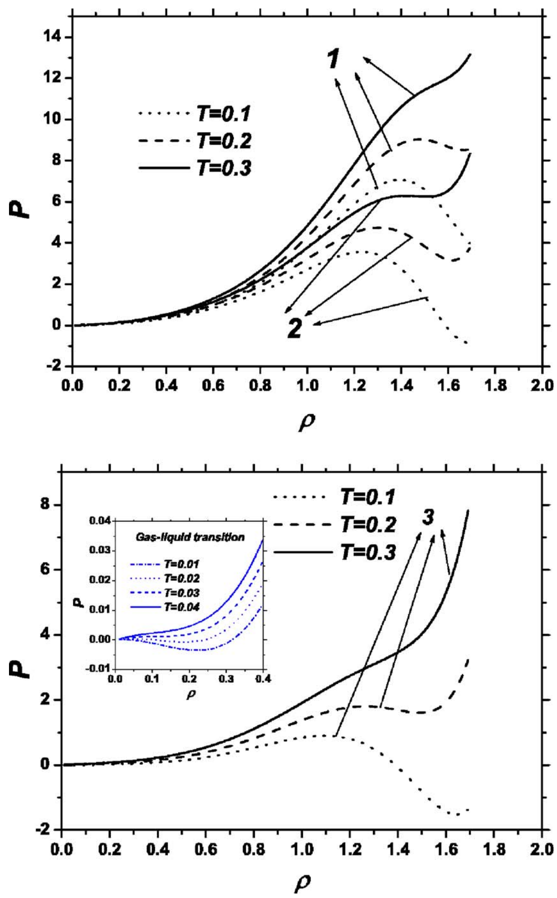

FIG. 7. (Color online) The families of isotherms corresponding to the potentials in Fig. 6. There are only high-density fluid-fluid transitions for the potentials corresponding to lines 1 and 2 in Fig. 6 (upper figure). For the potential corresponding to the line 3 in Fig. 6, there is also a low-temperature gas-liquid transition shown in the inset in the lower figure.

$$\Phi_0(r) = b\left(\frac{\sigma}{r}\right)^{18}. \quad (7)$$

Potential $\Phi_0(r)$ is approximated by the hard sphere potential with an effective diameter which depends on the density and the temperature [34,37].

From Fig. 7 one can see that there are only high-density fluid-fluid transitions for the potentials corresponding to the lines 1 and 2 in Fig. 6 (upper figure). These transitions exist due to negative curvature of the potential (6). There are no low density (i.e., gas-liquid) transitions in these cases because the strength of an attraction is insufficient. For the potential corresponding to line 3 in Fig. 6 there is also a gas-liquid transition at low temperatures shown in the inset in the lower figure.

IV. CONCLUSIONS

The main purpose of the present investigation is to develop the simple almost analytical approach for the qualitative description of the properties of systems with the repulsive soft-core attractive potential (1), and on the basis of this approach, to study the physical mechanism underlying the possible liquid-liquid phase transition in these systems. In the framework of the first order thermodynamic perturbation theory we have studied the phase diagrams of these systems for different values of potential parameters, and in agreement with the results of Refs. [27,28], have shown that there are some regions in the parameter space where the high-density critical point can exist in addition to the gas-liquid critical point.

We have considered two different ways of variation of the potential parameters. In the former case the overall length of the potential is fixed and in the latter case the width of the attractive well is constant. In both cases the width of the repulsive step σ is variable. In the framework of the second case we have also considered the system with a purely repulsive step potential which corresponds to the repulsive soft-core attractive potential (1) with zero width of the attractive well and have shown that in this system there is a high density fluid-fluid phase transition for some ranges of the repulsive step width. We have found some kind of periodic behavior of the phase diagram as a function of repulsive step radius σ which apparently correlates with the behavior of the radial distribution function $g_{HS}(r)$. This behavior may be explained by the analysis of the dependence of the free energy (2) on the repulsive step radius σ. This scenario strongly correlates with the case when the attractive well is added to the potential where phase diagrams demonstrate similar "periodic" behavior as a function of the repulsive step radius σ, as one can see in Fig. 4. It should be specially noted that the attractive well not only leads to the gas-liquid phase transition but also considerably stabilizes the liquid-liquid phase transition: the critical temperature of the liquid-liquid phase transition in the presence of the attractive well is much higher than the very low critical temperature of the fluid-fluid phase transition in the underlying purely repulsive step potential system. This means that it could be difficult or even impossible to find a fluid-fluid phase transition in the purely repulsive step potential systems in computer simulations, but, as was shown in Refs. [17,18,27,28], it can be found when the attractive well is present.

In the framework of the first order perturbation theory for solids [39–42] we have estimated the locations of the solid-liquid transition lines and have shown that for larger values of σ one can expect that the liquid-liquid phase transition may occur in the stable fluid region.

As an illustration of our approach we have also considered the soft potential which qualitatively resembles the effective potentials of some metals and have shown that two critical points may exist in these systems for some sets of the potential parameters.

We would like to emphasize that we do not claim that the first order perturbation scheme, which was used in the present article, gives the high precision quantitative results, however, it seems reliable enough to give correct qualitative description of the liquid-liquid transition in the system with potentials (1) and (6). It should be noted that the second-order perturbation theory gives qualitatively the same results [31,32].

ACKNOWLEDGMENTS

We thank S. M. Stishov, V. V. Brazhkin, and A. G. Lyapin for stimulating discussions. The work was supported in part by the Russian Foundation for Basic Research (Grant Nos. 05-02-17280 and 05-02-17621) and NWO-RFBR Grant No. 047.016.001.

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