Repulsive step potential: A model for a liquid-liquid phase transition

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In the framework of the perturbation theory for fluids we study the model with the isotropic repulsive step potential which in addition to the hard core has a repulsive soft core of a larger radius. It is shown that this purely repulsive potential is sufficient to explain a liquid-liquid phase transition and liquid anomalies.

It has been known for many years that a system of hard spheres experiences the only phase transition at a high density, when $\sigma \approx l$, where σ is the hard sphere diameter, $l = (V/N)^{1/3}$ is the average interparticle distance (V is the system volume, N is the number of particles). This transition corresponds to the ordering of the centers of gravity of the particles and may be called an order-disorder transition or crystallization. In the case of hard particles of different shapes such as hard rods, ellipses, discs, etc., a number of orientational phase transitions may occur in accordance with a hierarchy of characteristic lengths, which are defined by particle shapes. A new situation arises when an extra interaction of finite amplitude ε is added to a system of hard particles. As it is known from van der Waals theory, a negative value of ε inevitably causes an instability of the system in a certain range of density and generally leads to a first-order phase transition with no symmetry change (the order parameter, characterizing this transition is simply the density difference of the coexisting phases: $\Delta \rho = \rho_1 - \rho_2$). This situation is almost universal and doesnot depend on the interaction length.

Much less is known about a case when the interaction parameter ε has a positive value. The simplest example of that kind of interaction is the so-called repulsive step potential

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

Thereafter we will call a system of particles interacting via the potential (1): a system of "collapsing" hard spheres [1]. This kind of system is studied in connection with anomalous melting curves, isostructural phase transitions, transformations in colloid systems, etc. (see, for example, Refs. [2–6]). A general conclusion derived from numerous studies of the system is that the repulsive interaction of finite amplitude and length results in the melting curve anomaly and the isostructural solid-solid phase transition. The latter is a first-order phase transition and may end in the critical point, since there is no symmetry change across the phase transition line. The existence of that kind of a phase transition is a direct consequence of the form of the interparticle interaction and we do not see any particular reason why it cannot occur in a fluid phase.

It is widely believed (see, for example, Refs. [7,8]) that a fluid-fluid transition should be related to the attractive part of the potential. In the present paper we show that the purely repulsive step potential (1) is sufficient to explain a liquid-liquid phase transition and anomalous behaviors of the thermal expansion coefficient.

We apply to the problem the second-order thermodynamic perturbation theory for fluids. The soft core of the potential (1) is treated as perturbation with respect to the hard sphere potential. In this case the free energy of the system may be written in the form [9,10]

$$\frac{F - F_{HS}}{N k_B T} = \frac{1}{2} \rho \beta \int u_1(r) g_{HS}(r) d\mathbf{r} - \frac{1}{4} \rho \beta^2 \left[k_B T \left(\frac{\partial \rho}{\partial P} \right)_0 \right]$$

$$\times \int [u_1(r)]^2 g_{HS}(r) d\mathbf{r}, \tag{2}$$

where $\rho = V/N$ is the mean number density, $\beta = 1/k_B T$, $u_1(r)$ is the perturbation part of the potential $u_1(r) = \Phi(r) - \Phi_{HS}(r)$, $\Phi_{HS}(r)$ is the hard sphere singular potential, $g_{HS}(r)$ is the hard sphere radial distribution function, which is taken in the Percus-Yevick approximation [11]. In the same approximation the compressibility can be written in the form [10]

$$k_B T \left(\frac{\partial \rho}{\partial P} \right)_0 = \frac{(1 - \eta)^4}{(1 + 2\eta)^2}. \tag{3}$$

To calculate F_{HS}, one can use, for example, the approximate equation [10]

$$\frac{F_{HS}}{k_B T N} = 3 \ln \lambda - 1 + \ln \rho + \frac{4\eta - 3\eta^2}{(1 - \eta)^2}. \tag{4}$$

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

Further in this paper we use the dimensionless quantities: $\widetilde{P} = P \sigma^3 / \varepsilon$, $\widetilde{V} = V/N \sigma^3 = 1/\widetilde{\rho}$, $\widetilde{T} = k_B T / \varepsilon$, omitting the tilde marks. Results of the calculations are demonstrated in Figs. 1 and 2. In Fig. 1 a family of pressure isotherms is shown for the system with $\sigma_1 / \sigma = 1.5$. The van der Waals loops in the isotherms at low temperatures are clearly seen, this indicates the existence of the first-order liquid-liquid phase transition. A critical point is found at $T_c \approx 0.21, V_c \approx 1.015$.
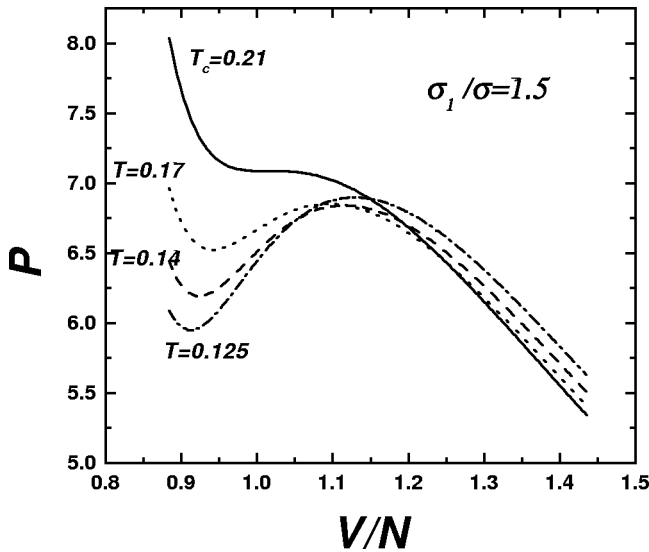
FIG. 1. Compression isotherms of the collapsing sphere system at various temperatures (dimensionless units).

An interesting and unusual feature of the isotherms in Fig. 1 is their intersection in the low-density region. This kind of behavior means negative value of the thermal expansion coefficient in the certain region of density and temperature. In Fig. 2 the thermal expansion coefficient $\alpha_P = V^{-1}(\partial V/\partial T)_P$ is shown as a function of temperature for two values of specific volumes $V_1 = 0.85$ and $V_2 = 1.25$, corresponding to the high-density and low-density liquids, respectively. One can see that in the case of the low-density liquid there is a range of negative values of α_P below the critical temperature.

Using the Maxwell construction we were able to calculate the equilibrium lines of the liquid-liquid phase transitions at different values of σ_1/σ (Fig. 3). We cannot extend the transition lines down to zero temperature because of limitation of the perturbation approach.
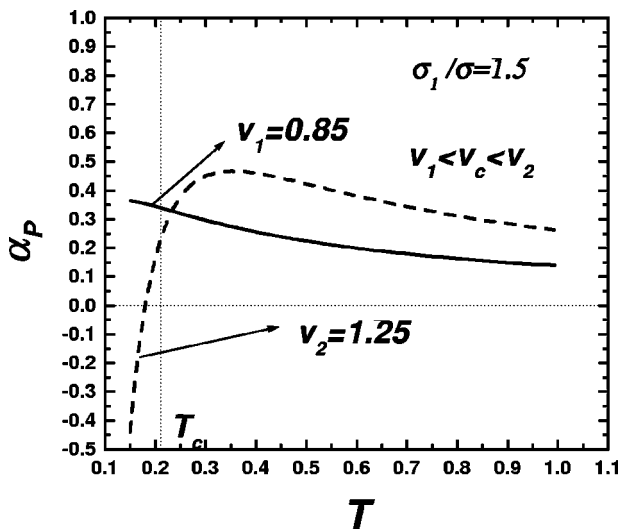

FIG. 2. The thermal expansion coefficient α_P as a function of temperature for two values of specific volumes $V_1 = 0.85$ and $V_2 = 1.25$, $V_1 < V_c < V_2$ (dimensionless units).
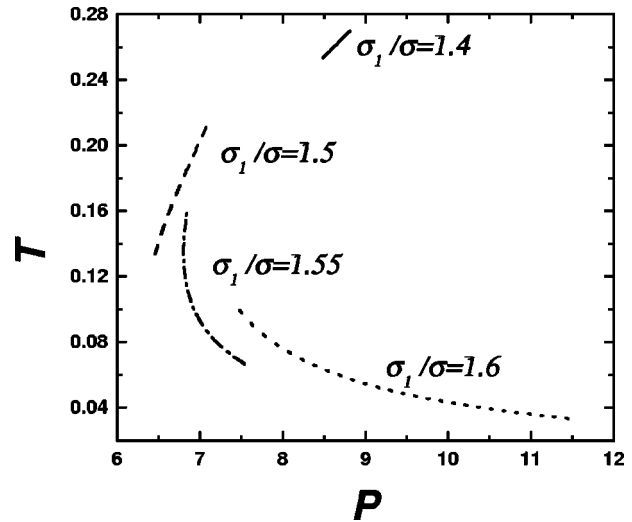

FIG. 3. Phase diagram of the liquid-liquid phase transition for different values of σ_1/σ (dimensionless units).

One can see from Fig. 3 that (1) the critical temperature decreases when the ratio σ_1/σ increases and (2) the slope of the transition curves changes drastically with changes in the ratio σ_1/σ and temperature. Decrease of the critical temperature may suggest that the transition ceases to exist at high values of the ratio σ_1/σ. It is not surprising since at long-range interaction perturbation energy can be treated in the mean field approximation. In this case the perturbation energy is a positive monotonic function of volume ($\delta F \propto 1/V$), and cannot provide any ground for the existence of a phase transition. The change of the slope of the transition line means in accordance with the Clausius-Clapeyron equation $dT/dP = \Delta V/\Delta S$ (ΔV and ΔS are change of volume and entropy at transition) that the entropy jump at the transition changes sign for different values of the ratio σ_1/σ and temperature. This behavior of the entropy change can be possibly understood in the terms of the entropy of mixing, meaning that two states of the particles of the system may be considered as two different species.

To elucidate the nature of the transition it is instructive to estimate the coefficient of surface tension between two liquid phases $\gamma(T)$. In the case of a liquid-liquid transition it is convenient to use the simple equation which is the generalization of the well-known equations obtained by Fowler, Kirkwood, and Buff [12–14]:

$$\gamma(T) = \frac{\pi}{8} \int_0^\infty dr\, r^4 \Phi'(r) \tilde{\rho}_2(r), \qquad (5)$$

where

$$\tilde{\rho}_2(r) = (\rho_{l_1}\sqrt{g_{l_1}(r)} - \rho_{l_2}\sqrt{g_{l_2}(r)})^2, \qquad (6)$$

ρ_{l_i} and $g_{l_i}(r)$ are the density and the radial distribution function of the ith phase [15].

In the approximation corresponding to the second-order perturbation theory (2), the radial distribution function $g_{l_i}(r)$ can be written in the form [10]

$$g_{l_i}(r) = \begin{cases} g_{HS}(r)\exp\left(-\dfrac{1}{T}\dfrac{(1-\eta_i)^4}{(1+2\eta_i)^2}\right), & r<\sigma_1 \\[2mm] g_{HS}(r), & r\geq\sigma_1. \end{cases} \quad (7)$$

It should be noted that Eq. (7) gives qualitatively correct description of two-peak structure of the radial distribution function of the system with the potential (1).

Approximations (5)–(7) are rather crude, but we believe that they at least qualitatively correctly describe the behavior of surface tension as a function of temperature and pressure.

Using Eq. (1) we rewrite Eq. (5) in the form

$$\gamma(T) = \frac{\pi}{8}[\sigma^4\varepsilon\widetilde{\rho}_2(\sigma) - k_BT\sigma^4\widetilde{\rho}_2(\sigma) - \sigma_1^4\varepsilon\widetilde{\rho}_2(\sigma_1)]. \quad (8)$$

From Eq. (8) one can see that in the case of hard sphere potential surface tension coefficient $\gamma(T)$ is always negative, however, it may become positive for the potential (1) due to the first term in the right-hand side of Eq. (8). It should be noted that it is the last term of Eq. (8) that explains the decrease of critical temperature of liquid-liquid transition with increasing σ_1 (see Fig. 3).

In Fig. 4 we show the dimensionless surface tension coefficient $\widetilde{\gamma}(T) = \gamma\sigma^2/\varepsilon$ as a function of dimensionless temperature $\widetilde{T} = k_BT/\varepsilon$ for two ratios $\sigma_1/\sigma = 1.5$ and $\sigma_1/\sigma = 1.6$ (the tilde marks are omitted).These curves are calculated along the corresponding curves in Fig. 3. From Fig. 4 one can see that the coefficient of surface tension is positive and tends to zero as temperature approaches T_c. So that the liquid-liquid phase transition in the system with purely repulsive step potential is a true first-order phase transition and occurs through nucleation and growth of the new phase.

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

The liquid-liquid transition line found lies most probably below the melting curve and may be observed only in meta-
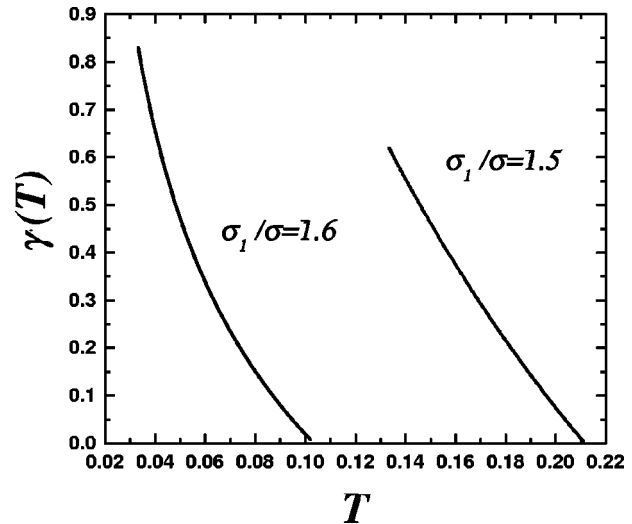

FIG. 4. Dimensionless surface tension coefficient $\gamma(T)$ as a function of dimensionless temperature T for two ratios $\sigma_1/\sigma = 1.5$ and $\sigma_1/\sigma = 1.6$.

stable liquid state, like it was discovered in the supercooled water [16,17]. Though in some cases the liquid-liquid transition may be observed in stable liquids [18,19].

Note that one would expect to get second phase transition, corresponding to the liquid-gas transformation, when an attractive tail is appended to the repulsive step potential, as it was seen in the molecular dynamic calculations [20,21]. We perform corresponding calculations using the second-order perturbation scheme with the core-softened potential proposed by Stanley and co-authors [20,21] and found second phase transition and second critical point. That may be viewed as some sort of justification of our approach to phase transformations in liquids.

Finally, we found essential evidences for a first-order phase transition in the liquid state of a system of collapsing hard spheres.

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$$z_1 > 0, \quad z_2 > 0,$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_{l_1}^2 g_{l_1}(r),$$

$$z_1 < 0, \quad z_2 < 0,$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_{l_2}^2 g_{l_2}(r),$$

$$z_1 > 0, \quad z_2 < 0 \quad \text{or} \quad z_1 < 0, \quad z_2 > 0,$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_{l_1} \rho_{l_2} \sqrt{g_{l_1}(r) g_{l_2}(r)}.$$

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