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A LIQUID–LIQUID PHASE TRANSITION IN THE «COLLAPSING» HARD SPHERE SYSTEM

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A liquid–liquid phase transition is discovered in a system of collapsing hard spheres using the thermodynamic perturbation theory. This is the first evidence in favor of the existence of that kind of phase transitions in systems with purely repulsive and isotropic interactions.

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It has been known for many years that the system of hard spheres experiences the only phase transition at a high density, when $\sigma \approx l$, where σ is the hard sphere diameter and $l = (V/N)^{1/3}$ is the average interparticle distance (V is the system volume and N is the number of particles). This transition corresponds to the ordering of the centers of gravity of the particles and can be called an order–disorder transition, or crystallization. In case of hard particles of different shapes such as hard rods, ellipses, discs, etc., a number of orientational phase transitions can occur in accordance with a hierarchy of characteristic lengths defined by particle shapes. A new situation arises when an extra interaction of a finite amplitude ε is added to the system of hard particles. As known from the van der Waals theory, a negative value of ε inevitably causes an instability of the system in a certain range of densities 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 independent of the interaction length.

Much less is known about the case where the interaction parameter ε has a positive value. The simplest example of an interaction of that kind is the so-called repulsive step potential (Fig. 1):

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

In what follows, the system of particles interacting via potential (1) is called the system of «collapsing» hard spheres [1]. Systems of this type are studied in relation to anomalous melting curves, isostructural phase transitions, transformations in colloid systems, etc. (see, e.g., [2–5]). 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 can end in a critical point, because there is no symmetry change across the phase transition line. The existence of a phase transition of that type is a direct consequence of the form of the interparticle interaction and we see no particular reason why it cannot occur in a fluid phase.

Despite the growing interest in the possible polymorphic phase transitions in liquids and glasses (see, e.g., for [6] recent reviews), the nature of different phases that can be found in dense (and possibly metastable) liquids is still puzzling. In recent years, experimental evidence of such features of the phase di-

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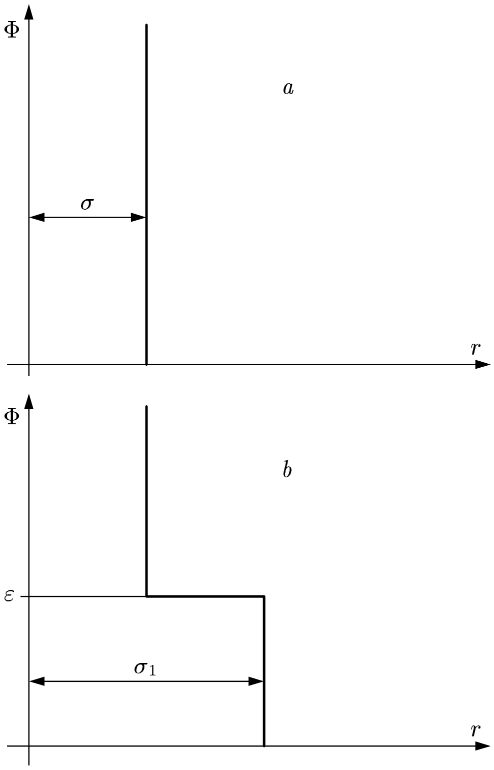

Fig. 1. *a*) The hard-sphere potential with the hard-sphere diameter σ. *b*) The repulsive step potential; σ is the hard-core diameter, σ_1 is the soft-core diameter, and ε is the height of the repulsive step

agram as liqiud–liquid transitions, polymorphism, etc. appeared for a wide range of systems including water, Si, I, Se, S, C, P, etc. [6]. The complexity of the phase diagrams in these substances may result from complex interactions depending on the intermolecular orientations. At the same time, exploring the possibility that simple fluids interacting through isotropic potentials may exhibit a similar behavior represent a serious challenge for theorists.

The possibility of the existence of a liquid–liquid phase transition drastically depends on the shape of the interparticle potential. After the pioneering work by Hemmer and Stell [2], much attention has been paid to investigating the properties of the systems with the so-called core-softened potentials — the potentials that have a negative curvature region in their repulsive core. It has been shown that depending on the parameters of the potentials, waterlike thermodynamic anomalies and the second critical point can be observed in this system [6–10]. It is widely believed, however (see, e.g., [7, 8]), that the existence of a fluid–fluid transition must be related to the attractive part of the potential. In this paper, we show that the purely repulsive step potential in Eq. (1) is sufficient to explain a liquid–liquid phase transition and the anomalous behavior of the thermal expansion coefficient.

We apply the second-order thermodynamic perturbation theory for fluids to this problem. The soft core of potential (1) (Fig. 1*b*) is treated as a perturbation with respect to the hard sphere potential (Fig. 1*a*). In this case, the free energy of the system can be written as [11, 12]:

$$\frac{F-F_{HS}}{Nk_BT} = \frac{1}{2}\rho\beta\int u_1(r)g_{HS}(r)d\mathbf{r} - \\ - \frac{1}{4}\rho\beta^2\left[k_BT\left(\frac{\partial\rho}{\partial P}\right)_0\right] \times \\ \times \int [u_1(r)]^2 g_{HS}(r)d\mathbf{r}, \quad (2)$$

where $\rho = V/N$ 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 [13]. In the same approximation, the compressibility can be written as [12]

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

We note that the actual small parameter in expansion (2) is the ratio $\varepsilon/(k_BT)$, and therefore, the perturbation scheme used in this paper works very well at high temperatures and gives quantitative agreement with computer simulations for intermediate temperatures and sufficiently high densities [11, 12]. We believe that in the range of temperatures and densities considered in this paper, Eq. (2) gives correct results at least qualitatively.

To calculate F_{HS}, we can use, e.g., the approximate equation [12]:

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

where $\lambda = h/(2\pi mk_BT)^{1/2}$ and $\eta = \pi\rho\sigma^3/6$. In what follows, we use the reduced quantities $\tilde{P} = P\sigma^3/\varepsilon$, and $\tilde{V} = V/N\sigma^3 = 1/\tilde{\rho}$, $\tilde{T} = k_BT/\varepsilon$, omitting the tildas.

The results of the calculations are demonstrated in Figs. 2 and 3. In Fig. 2, a family of pressure isotherms is shown for the system with $\sigma_1/\sigma = 1.5$. The van der Waals loops in the isotherms are clearly seen at low temperatures, indicating the existence of a first-order

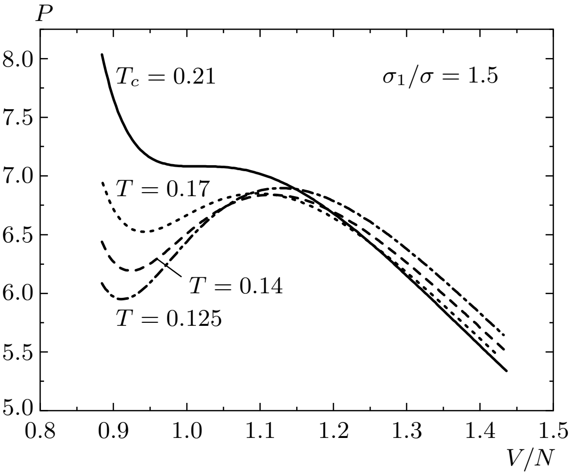

Fig. 2. Compression isotherms of the collapsing sphere system at various temperatures

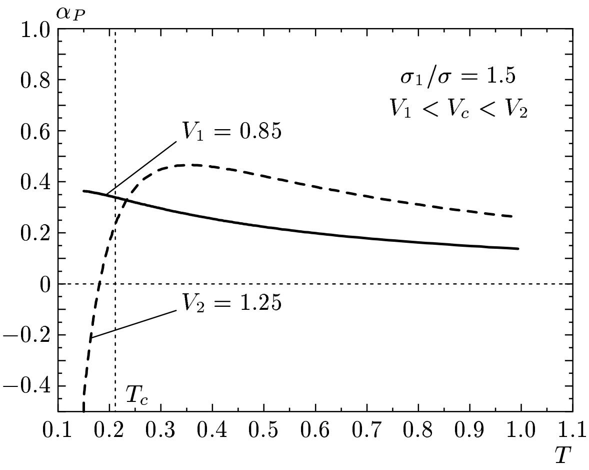

Fig. 3. The thermal expansion coefficient α_P as a function of temperature for two values of specific volume $V_1 = 0.85$ and $V_2 = 1.25$, $V_1 < V_c < V_2$

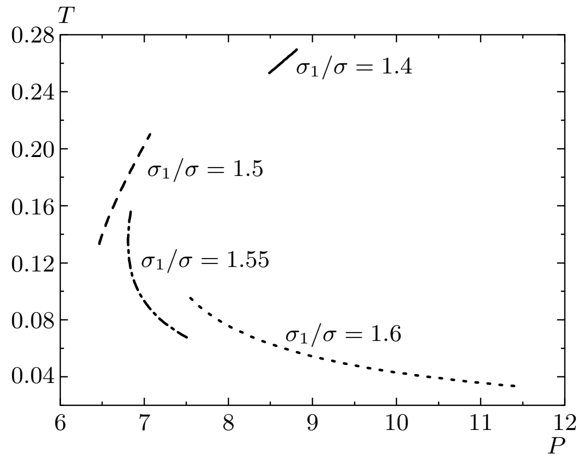

Fig. 4. Phase diagram of the liquid–liquid phase transition for different values of σ_1/σ

liquid–liquid phase transition. A critical point is found at $T_c \approx 0.21$ and $V_c \approx 1.015$.

An interesting and unusual feature of the isotherms in Fig. 2 is their intersection in the low-density region. This behavior implies negative value of the thermal expansion coefficient in the certain region of density and temperature. Most liquids contract upon cooling. But this is not the case for the most important liquid on Earth, water. It is well known that the specific volume of water increases when cooled below $T = 4C$. The existence of this anomaly can be related to the hypothetical liquid–liquid phase transition in supercooled water [14, 15]. This anomaly is not restricted to water but is also present in other liquids [16].

In Fig. 3, the thermal expansion coefficient $\alpha_P = V^{-1}\left(\partial V/\partial T\right)_P$ is shown as a function of the temperature for two values of specific volume $V_1 = 0.85$ and $V_2 = 1.25$, corresponding to the high-density and low-density liquids respectively. We can see that for the low-density liquid, there is a range of negative values of α_P below the critical temperature. The appearance of the negative thermal expansion coefficient can easily be understood for repulsive step potential (1). At low temperatures and densities, the particles do not penetrate the soft core of the potential. As the temperature increases, the particles can penetrate the soft core, and the average distance between particles can therefore decrease, resulting in the anomalous behavior of α_P. At high densities, this process is less pronounced because most of the particles are inside the soft core due to the external contraction. It must be noted that Stillinger and collaborators also found a negative thermal expansion coefficient $\alpha_P < 0$ for a purely repulsive Gaussian potential [17, 18] , but without a liquid–liquid transition.

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. 4). We cannot extend the transition lines to zero temperature because of the limitations of the perturbative approach. We can see from Fig. 4 that the critical temperature decreases as the ratio σ_1/σ increases and the slope of the transition curves drastically changes with changes of the ratio σ_1/σ and the temperature. The decrease of the critical temperature may suggest that the transition ceases to exist at high values of the ratio σ_1/σ. This is not surprising because for a longrange interaction, perturbation energy can be treated in the mean-field approximation. The perturbation energy is then a positive monotonic function of the volume ($\delta F \propto 1/V$) and cannot provide any ground for the existence of a phase transition. In accordance with the Clausius–Clapeyron equation $dT/dP = \Delta V/\Delta S$ (where ΔV and ΔS are the variations of volume and entropy at the transition), the change of the slope of the transition line implies that the entropy jump at the transition changes its sign for different values of the ratio σ_1/σ and the temperature. This behavior of the entropy change can possibly be understood in the terms of the entropy of mixing, implying that two states of particles in the system can be considered as two different species.

The liquid–liquid transition line found most probably lies below the melting curve and can be observed only in the metastable liquid state, as was discovered in supercooled water [14, 15]. On the other hand, the liquid–liquid transition can be observed in stable liquids in some cases [6, 19, 20]. It must be noted that computer simulations also show [8] that for some choices of the parameters of the potential (and in the presence of the attractive part of the potential), a liquid–liquid phase transition can occur in the stable range of the phase diagram.

We note that a second phase transition corresponding to the liquid–gas transformation can be expected when an attractive tail is appended to the repulsive step potential, as was observed in the molecular dynamic simulations [9, 10]. We performed the corresponding calculations using the second-order perturbation scheme with the parameters of the core-softened potential proposed by Stanley and coauthors [9, 10] and found a second phase transition and a second critical point. That may be viewed as some sort of justification of our approach to phase transformations in liquids.

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

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