

Silicalike sequence of anomalies in core-softened systems

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We present a simulation study of density, structural, and diffusion anomalies in a core-softened system, a remarkable model liquid that exhibits anomalous properties seen in tetrahedral liquids such as silica and water. It is widely believed that core-softened potentials demonstrate waterlike sequence of anomalies. Here, we show that the order of the region of anomalous diffusion and the regions of density and structural anomalies are inverted with increasing depth of the attractive part of the potential and have silicalike sequence. We also show that the Widom line slope is negative as in water.

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I. INTRODUCTION

In past decades, there was a growing interest in the class of liquids displaying anomalous thermodynamic and kinetic behaviors. The most common and well-known example of such behavior is water. The water phase diagram has regions where the thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly) [1–6]. Later, it was discovered that many other substances also demonstrate similar behavior. Some typical examples are silica, silicon, and phosphorus [5–11].

As found in experiments [1] and simulations [3,4], the water anomalies have a well-defined sequence: The regions where these anomalies take place form nested domains in the density-temperature [3] (or pressure-temperature [4]) planes, the density anomaly region is located inside the diffusion anomaly domain, and both of these anomalous regions are located inside a broader structurally anomalous region. This waterlike behavior was found in systems with spherically symmetric core-softening potentials with two length scales [12–28].

However, in other anomalous systems, the sequence of anomalies may be different. For example, in computer simulation of the system with the Van Beest–Kramer–Van Santen (BKS) potential, the hierarchy of anomalies in silica is different than in water [7]. In this case, the diffusion anomaly region contains the structurally anomalous region which, in turn, incorporates the density anomaly region. To our knowledge, this is the only example of such an inversion of the order of the anomalies discussed in the literature until now.

It is widely believed that in the core-softened systems the hierarchy of anomalies is of the waterlike type. For example, Yan *et al.* [18,19] characterized the structural, thermodynamic, and kinetic properties of a family of discontinuous core-softened potentials that vary in the length scale of the soft repulsion region. In each case, they found the same relationship between anomalous regions as observed in water: Structural anomalies preceded diffusivity anomalies, which in turn preceded density anomalies. Reference [20] discussed an approach to analysis of anomalous behavior based on the well-known Rosenfeld scaling relations [29], which relate the transport coefficients to

excess entropy. In this case, the explicit equation determining the appearance of the anomalies in the system was obtained [20]:

$$\left(\frac{\partial S_{\text{ex}}}{\partial \ln \rho} \right)_T > c, \quad (1)$$

where ρ is the number density, $S_{\text{ex}} = S - S_{\text{id}}$ is the excess entropy, equal to the difference between the total S and ideal gas S_{id} entropies, and c is the property-specific constant. Based on Rosenfeld scaling parameters [20], it was shown that the value $c = 0$ corresponds to the structural anomaly, $c = 0.42$ corresponds to the diffusion anomaly, and $c = 1$ corresponds to the density anomaly. It can be seen from Eq. (1) that the anomalous behavior always occurs in the waterlike order: Structural anomalies precede diffusivity anomalies, which in turn precede density anomalies. This conclusion was verified by computer simulations of the system interacting through the two-scale potential introduced by Jagla [30,31]. However, as was shown in our previous papers [24,26], the Rosenfeld scaling is invalid in the vicinity of anomalies and cannot be used for correct analysis of the order of anomalies.

It is important to note that Eq. (1) contains two conditions which are based on strict thermodynamic arguments, namely the conditions for structural and density anomalies [20]. This means that the density anomaly must *always* follow after the structural anomaly. On the other hand, the diffusion anomaly can be located at any place. For example, in silica the diffusion anomaly precedes the structural and density anomalies.

This paper presents a simulation study of anomalies in the core-softened system introduced in our previous publications [21–28]. We investigate the sequence of anomalous regions and find that, with increasing the attractive part of the potential, the system demonstrates both waterlike and silicalike behavior. It is also shown that qualitatively the potential correctly reproduces the behavior of the Widom line of the system.

II. SYSTEMS AND METHODS

In the present study, we investigate a system of particles interacting via the potential with the “hard” core, repulsive shoulder, and attractive well [22,26].

TABLE I. The potential parameters used in the simulations [Eq. (2)].

Number	σ_1	σ_2	λ_0	λ_1	λ_2	Well depth
1	1.35	0	0.5	0.5	0	0
2	1.35	1.80	0.5	0.60	0.10	0.20
3	1.35	1.80	0.5	0.7	0.20	0.4

The general form of the potential is written as

$$U(r) = \varepsilon \left(\frac{\sigma}{r} \right)^{14} + \varepsilon [\lambda_0 - \lambda_1 \tanh(k_1 \{r - \sigma_1\}) + \lambda_2 \tanh(k_2 \{r - \sigma_2\})]. \quad (2)$$

Here $k_1 = k_2 = 10.0$, and the parameters of Eq. (2) are given in Table I. The family of potentials with $\sigma_1 = 1.35$ and different attractive wells is shown in Fig. 1. It should be noted that potential (2) is very similar to the Fermi-Jagla potential suggested recently in Ref. [32], where the Fermi distribution function is used instead of the hyperbolic tangent in Eq. (2) in order to describe the smoothed step [33,34].

In the remainder of this paper we use the dimensionless quantities $\tilde{\mathbf{r}} \equiv \mathbf{r}/\sigma$, $\tilde{P} \equiv P\sigma^3/\varepsilon$, $\tilde{V} \equiv V/N\sigma^3 \equiv 1/\tilde{\rho}$, $\tilde{T} \equiv k_B T/\varepsilon$. Since we use only these reduced variables, the tildes are omitted.

It was shown in Refs. [21–28] that these systems demonstrate anomalous behavior. The relationship between the phase diagram and the anomalous regions was also discussed [24–28]. In the present paper, we analyze changes in the phase diagram and anomalous regions, which are caused by changes of the potential parameters. The details of simulations can be found in Ref. [27].

In order to find the melting lines we calculate the free energies of different phases and use the common tangent construction. For our current potentials, we computed the free energy of the liquid by integrating the equation of state along the isotherm [35]: $\frac{F(\rho) - F_{id}(\rho)}{Nk_B T} = \frac{1}{k_B T} \int_0^\rho \frac{P(\rho') - \rho' k_B T}{\rho'^2} d\rho'$. The free energies of different crystalline phases were obtained by the Monte Carlo simulations with the method of coupling to

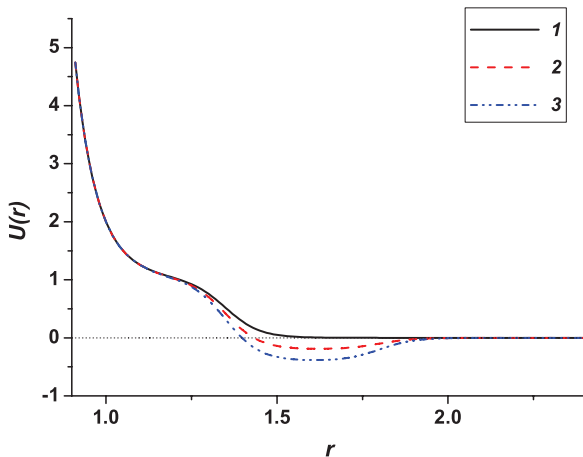


FIG. 1. (Color online) Family of the potentials with $\sigma_1 = 1.35$ and different attractive wells. The curves are numbered in accordance with Table I.

the Einstein crystal [35]. In this case the excess entropy can be computed via $S_{ex} = \frac{U - F_{ex}}{Nk_B T}$, where U is the internal energy [35]. The total entropy is $S = S_{ex} + S_{id}$, where the ideal gas entropy is $\frac{S_{id}}{Nk_B} = \frac{3}{2} \ln(T) - \ln(\rho) + \ln\left(\frac{(2\pi mk_B)^{3/2} e^{5/2}}{h^3}\right)$.

Here, we discuss the anomalous regions for the three systems shown in Fig. 1.

The density anomaly means that the density increases upon heating (the thermal expansion coefficient becomes negative). Using the thermodynamic relation $(\partial P/\partial T)_V = \alpha_P/K_T$, where α_P is the thermal expansion coefficient and K_T is the isothermal compressibility, and taking into account that K_T is always positive and finite for systems in equilibrium away from the critical point, we conclude that the density anomaly corresponds to the minimum of the pressure dependence on temperature along the isochore. This is the most convenient indicator of the density anomaly in computer simulations.

Initially, the structural anomaly was introduced via the order parameters characterizing the local order in a liquid [3,7,17,18,36–39]. However, later on the local order was also related to the excess entropy of the liquid, which is defined as the difference between the entropy and the ideal gas entropy at the same (ρ, T) point: $S_{ex} = S - S_{id}$. In normal liquids, the excess entropy is a monotonically decaying function of density along the isotherm, while in anomalous liquids it increases in a certain region of the thermodynamic parameters. This allows us to define the boundaries of the structural anomaly at a given temperature as the minimum and maximum of the excess entropy.

III. RESULTS AND DISCUSSION

The behavior of the diffusion coefficient, pressure, and excess entropy for the purely repulsive system with $\sigma_1 = 1.35$ has been discussed, for example, in Refs. [21,24,26–28]. One can see that all of the three anomalies take place in the system. Figure 2(a) shows the regions of the anomalies in the phase diagram. As it was shown in Refs. [21,22,27] (see, for example, Fig. 1 in Ref. [22]), the phase diagram of the system consists of the high-density and low-density face-centered-cubic (fcc) phases, corresponding to the hard core and repulsive shoulder parts of the potential, separated by a sequence of crystalline phases. In Fig. 2(a), we show the low-density part of the phase diagram with the fcc and fct (face-centered-tetragonal) phases.

One can see that the anomalous regions correspond to the picture proposed for water [3]; i.e., the diffusion anomaly region is located inside the structural anomaly and the density anomaly is located mainly inside the diffusion anomaly.

It was shown in Ref. [27] that in the system with the purely repulsive potential, the diffusion and density anomalies become inverted with respect to each other as the repulsive core diameter increases; i.e., the diffusion-anomaly region is located inside the density-anomaly one.

Further, we consider the influence of attraction on the anomalous behavior of the system. In this case, we study the system with step size $\sigma_1 = 1.35$ and different well depths (Table I and Fig. 1). One can see that with increasing depth of the attractive well, the sequence of anomalies also becomes inverted: For $w = 0$, we have the waterlike order of anomalies [see Fig. 2(a)], and at $w = 0.2$ the locations of the diffusion and

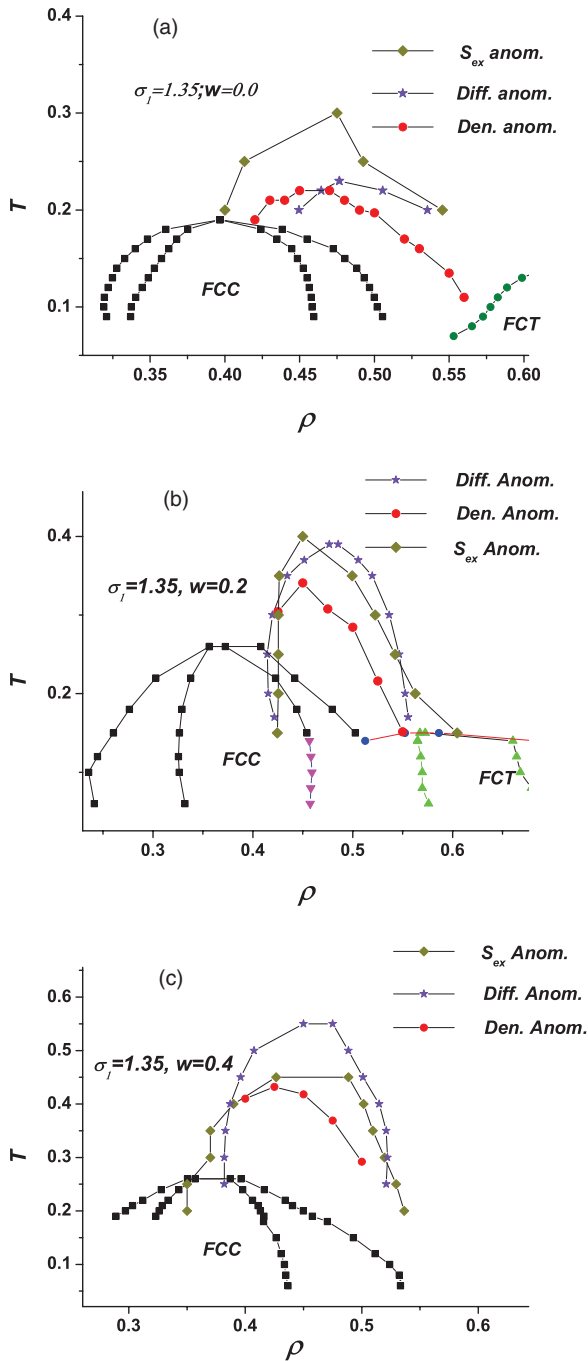


FIG. 2. (Color online) (a) Location of the anomalous regions in the low-density part of the phase diagram of the system with $\sigma_1 = 1.35$, where the fcc and fct phases are shown. The waterlike order of anomalies takes place: The density anomaly region is located inside the diffusion anomaly domain, and both of these anomalous regions are located inside a broader structurally anomalous region. (b) Location of the anomalous regions in the phase diagram for the system with $\sigma_1 = 1.35$ and $w = 0.2$; (c) the same for the system with $\sigma_1 = 1.35$ and $w = 0.4$ (the silicalike order of anomalies).

structural anomalies almost coincide [Fig. 2(b)]. Finally, for $w = 0.4$, the diffusion anomaly region contains the structural anomalous region which, in turn, has the density anomaly region inside [Fig. 2(c)] [40]. As a result, for $w = 0.4$, we

obtain the configuration of anomalies which is the same as in silica [7].

It seems that the most popular point of view is that the hypothesized liquid-liquid critical point (LLCP) is the thermodynamic source of all water anomalies [41–44]. LLCP is the terminal point of the line of first-order liquid-liquid phase transition. The line emanating from this critical point is sometimes called the Widom line and is often considered as an extension of the coexistence line into the one-phase region (see, for example, [32,41,46]). This line is determined by the lines of the maxima of the thermodynamic response functions, which asymptotically approach one another as the critical point is approached [41,46]. The lines of the liquid-liquid phase transition in the computer simulations of water [41] and silicon [45] have the negative slope. On the other hand, earlier computer simulations of the isotropic core-softened potentials (see, for example, Ref. [41]) suggested that the Widom line slope is positive in these systems.

Figure 3 shows the lines of the maxima of the isobaric heat capacity C_p along isobars and isotherms, the line of the maxima of the isothermal compressibility K_T , and the line of the minima of the thermal expansion coefficient α_p , along with the melting line for systems 2 and 3 (Table I). One can see, that for our potential, the Widom line has a slope which coincides with the results derived for water [41] and silicon [45]. It

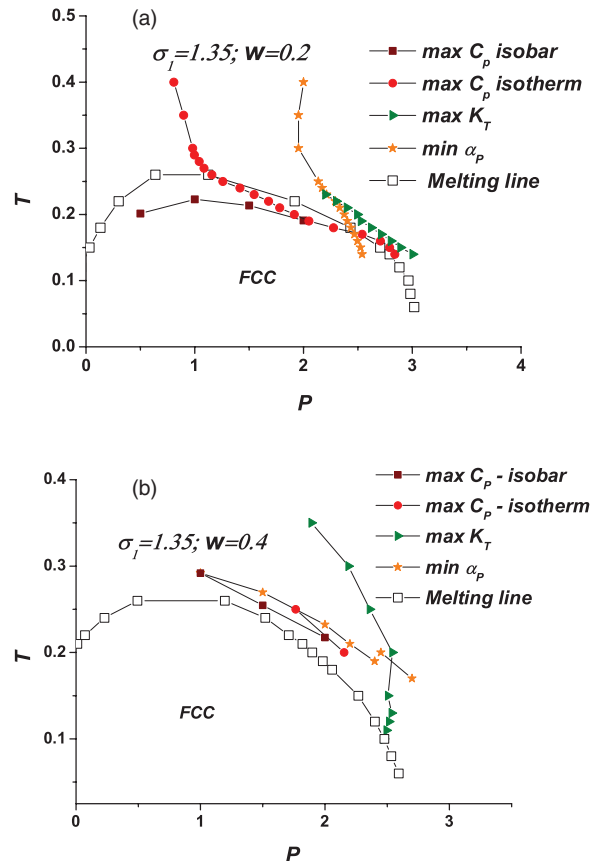


FIG. 3. (Color online) The maxima lines of isobaric heat capacity C_p along isobars and isotherms, the line of the isothermal compressibility maxima K_T , and the line of the thermal expansion coefficient α_p minima along with the melting line for the systems 2 (a) and 3 (b) (Table I).

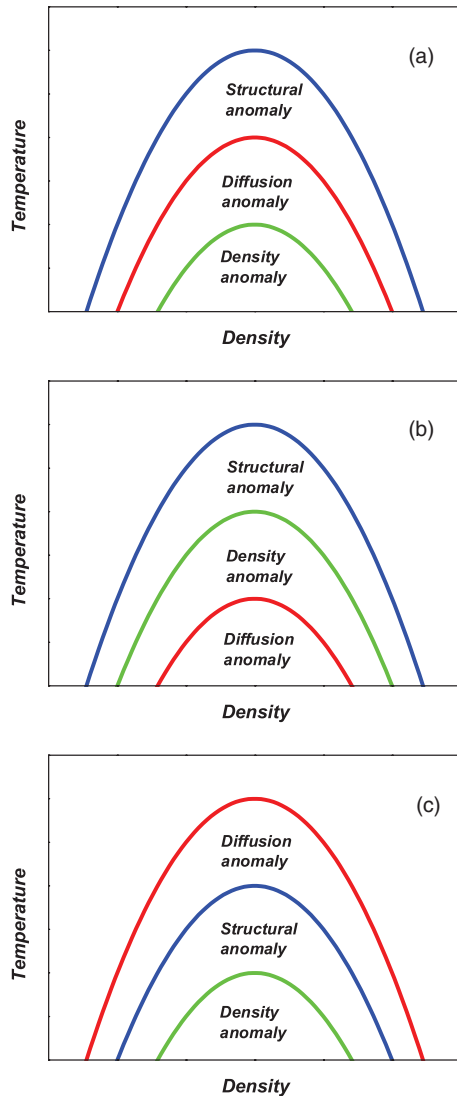


FIG. 4. (Color online) Schematic plot of regions where structural, diffusivity, and density anomalies are found within the temperature-density planes. The region of the anomalous density behavior always appears as a nested dome within the structural anomalous envelope, while the diffusivity anomaly may be located (a) between the structural and density ones (see Fig. 2) (waterlike behavior); (b) inside the density anomalous region; and (c) the outermost envelope (silicalike behavior).

should be noted that analogous results have been obtained recently [32] for the potential similar to Eq. (2).

IV. CONCLUSION

In conclusion, this paper presents a detailed computer simulation study of the anomalous behavior of core-softened systems proposed in our publications [21–28]. The

core-softened potentials are widely investigated because they reproduce waterlike anomalies. Taking into account that the anomalies also exist in systems where hydrogen bonds are absent, it seems that the unusual properties of water are quite universal and can be investigated with the aid of the isotropic core-softened potentials. To our knowledge, all isotropic core-softened potentials which were considered in the previous publications show the sequence of anomalies characteristic of water: The density-anomaly region is located inside the diffusion-anomaly domain, and both of these anomalous regions are located inside a broader structurally anomalous region. On the other hand, in other anomalous systems, the sequence of anomalies may be different. For example, the hierarchy of anomalies in silica is different than in water. In the present paper, we analyze the possibility of changing the order of anomalous regions depending on potential parameters. We emphasize, in contrast to Ref. [20], that there are only two conditions based on the strict thermodynamic arguments which show that the density anomaly must always follow after the structural anomaly. On the other hand, the diffusion anomaly can be located at any place depending on the form of the potential.

It is shown that for potential (2) with small values of the repulsive step the sequence of anomalies is the same as in water. However, with increasing width of the repulsive shoulder, the order of the region of anomalous diffusion and the region of density anomaly is inverted. With increasing depth of the attractive well, we obtain the configuration of anomalies which is the same as in silica [7], where the diffusion-anomaly region contains the structurally anomalous region, which, in turn, has the density-anomaly region inside. It appears to be the first case where the isotropic core-softened system demonstrates a sequence of anomalies which is different from those in water but potentially similar to silica. The schematic behavior of the anomalous regions is shown in Fig. 4. It should be noted that Figs. 4(a) and 4(c) correspond to the situations observed in real substances: water and silica. The case Fig. 4(b) may potentially correspond to some real substances, but they have not been observed so far.

It is also shown that for potential (2), the slope of the Widom line is negative as in water and silicon.

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