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Dynamical crossover in supercritical core-softened fluids

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ABSTRACT

It is well known that some liquids can demonstrate an anomalous behavior. Interestingly, this behavior can be qualitatively reproduced with simple core-softened isotropic pair-potential systems. Although the anomalous properties of liquids are usually manifested at low and moderate temperatures, it has recently been recognized that many important phenomena can appear in supercritical fluids. However, studies of the supercritical behavior of core-softened fluids have been not yet reported. In this work, we study dynamical crossover in supercritical core-softened systems. The crossover line is calculated from three different criteria, and good agreement between them is observed. It is found that the behavior of the dynamical crossover line of core-softened systems is quite complex due to its quasi-binary nature.

The most fundamental approach to the behavior of matter involves interactions between the particles of the substance. The most accurate approach is based on quantum mechanical treatment of interactions. However, such ab-initio methods require a lot of computational resources and cannot be applied to the systems larger than several hundreds of atoms. A great advance was made by application of so-called effective potentials. These potentials are constructed in such a way that they allow obtaining some principal properties of interest with much smaller efforts [1]. In the simplest case, the interaction is approximated by pair interactions only. One of the most studied systems is the Lennard-Jones (LJ) system which has the potential $U(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$. This system demonstrates a generic view of the phase diagram of a substance containing gas, liquid and crystal phases and well describes the behavior of noble gases and some molecular substances [2].

In our recent works, it was shown that supercritical region of the phase diagram can be divided into two parts: rigid liquid and dense gas [3–5]. These regions differ in the microscopic dynamics of particles and are separated by a crossover line called Frenkel line. The difference in microscopic dynamics leads to a number of consequences. In particular, close to the melting line liquids demonstrate transverse excitations and therefore they have non-zero shear rigidity at frequencies below the threshold one [5,6]. Basing on this we call this regime rigid liquid. On the other hand far from the melting line even in high pressure and high temperature limit the liquids do not demonstrate shear rigidity and behave like a gas. Therefore a term 'dense gas' is used to them. Later on, the phenomenon of dynamical crossover was studied for a number of other fluids [7–11].

Great attention of researchers is also focused on the anomalous behavior of liquids (see, e.g. Refs. [12], for the list of anomalies of water). Although anomalous properties were first discovered in water, many other liquids also demonstrate an anomalous behavior including liquids of very different natures: silicon [13], liquid silica [14], beryllium fluoride [15–17], some liquid metals [18], polymeric solutions [19], etc. Interestingly, it was found that models with isotropic pair core-softened potentials can demonstrate an anomalous behavior [20–27]. Diffusion, density and structural anomalies are widely discussed in the literature [28]. Such systems can also demonstrate numerous structural phase transitions in the solid region. This kind of behavior cannot be obtained in LJ-like systems. These observations make it possible to suppose that the behavior of the Frenkel line can also be more complex in the systems with core-softened potentials.

A particular form of core-softened systems studied in our previous works is characterized by the following interaction potential:

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$$U(r)/\varepsilon=\left(\frac{d}{r}\right)^n+\lambda_0-\lambda_1 th(k_1[r-\sigma_1])+\lambda_2 th(k_2[r-\sigma_2]), \qquad (1)$$

where d and ε spesify the length and energy scales, respectively, and λ_i and σ_i are varied. A large set of parameters was considered. It was found that the phase diagram and anomalous behavior of the system strongly depend on the parameters of the potential. An important feature of this system is its quasi-binary behavior, i.e., some features commonly observed in binary mixtures [20]. For example, the system can be easily vitrified [20,29]. The phase diagram of the system consists of a low density close packed FCC phase, a high density FCC phase and a set of intermediate structures, which can be considered as close packing of particles at a large length scale σ_1, a close packed structure at a small length scale d and a set of different structures in the region where the competition between these length scales takes place. Importantly, the low density FCC phase demonstrates a maximum of the melting line, a phenomena observed for many metals [30], but not in simple systems such as rare gases. The interplay between two length scales obviously affects the properties of the liquid too. Therefore, it is of interest to monitor the phenomena of dynamical crossover in the fluid for such a system. Moreover, the dynamic properties of binary mixtures were widely discussed in the literature and a complex behavior was discovered (see, e.g. Refs. [31–37], and references therein). This allows assuming that the quasi-binary system studied in this work can also demonstrate an unusual behavior.

The system with potential (1) has many unusual properties: a complex phase diagram with a maximum on the melting line and many different solid phases, anomalous density, diffusivity and structure, etc. For this reason, we believe that investigation of the dynamical crossover in this system will be helpful for understanding of the behavior of supercritical water and other anomalous fluids.

Two sets of the parameters of the potential (1) were studied: a purely repulsive system with the shoulder width $\sigma_1/d=1.35$ and a system with a repulsive shoulder and an attractive well. The parameters of the potentials are given in Table 1. The exponent in the first term of the potential is $n=14$ for both cases. Below, we refer to the systems with different parameters as "system 1" and "system 2". The potentials are shown in Fig. 1.

We measure all properties of the system in reduced units with respect to d and ε: $\tilde{\rho}=N/V\cdot d^3$, $\tilde{T}=k_BT/\varepsilon$, etc. Since only these reduced units are used in this work, we omit the tilde marks.

In all cases, systems of 1000 particles in a cubic box with periodic boundaries were simulated by a molecular dynamics method. The timestep was set to 0.0005 reduced units of time. The system was equilibrated by Ref. $3.5\cdot10^5$ steps followed by more $1.5\cdot10^5$ steps for data collection. During the equilibration run, the temperature was held constant by a Nose–Hoover thermostat. The production run was made in the *NVE* ensemble. All simulations were performed with the LAMMPS simulation package [38].

Several criteria can be used to determine the dynamical crossover line [3–5]. The velocity autocorrelation function (VACF) criterion and the isochoric heat capacity criterion [5] are among the most convenient criteria.

The velocity autocorrelation function is defined as $Z(t)=\frac{1}{3N}\langle\sum\frac{\mathbf{V}_i(t)\mathbf{V}_i(0)}{\mathbf{V}_i(0)^2}\rangle$ where $\mathbf{V}_i(t)$ is the velocity of the i-th particle at the time t. The VACFs of rigid fluids demonstrate an oscillatory behavior, whereas the VACFs of dense gases decease monotonically. Therefore, the Frenkel line corresponds to the (ρ,T) points where oscillations disappear [5].

Table 1
Parameters of potential (1) used in this study.

System no.	σ_1	σ_2	λ_0	λ_1	λ_2
1	1.35	0	0.5	0.5	0
2	1.35	1.8	0.5	0.7	0.2

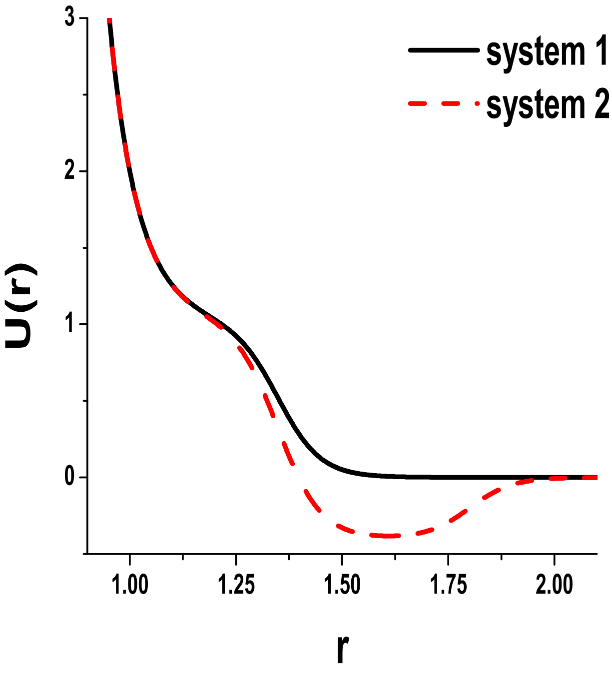

Fig. 1. (Color online) Interaction potentials studied in this work (eq. (1)).

The isochoric heat capacity criterion states that the Frenkel line is a line at which the isochoric heat capacity per particle is $c_v=2k_B$. It is based on the counting inclusion of contributions to the heat capacity of the liquid from longitudinal and transverse excitations. A detailed theory of the heat capacity of the liquid based on excitation spectra was proposed in recent works [39–41]. One can show that the contribution to the heat capacity from the potential energy of transverse modes in the rigid regime is 1 k_B per particle. At the Frenkel line, transverse excitations disappear and, therefore, the heat capacity per particle at the Frenkel line should be close to $2k_B$.

The crossover between different regimes of the fluid can also be identified by the appearance of strong positive sound dispersion (PSD). Positive sound dispersion means that the velocity of excitations in liquids at a certain finite wavelength k exceeds the adiabatic speed of sound c_s. Positive sound dispersion was experimentally observed in a number of low-temperature fluids (see, e.g. Refs. [42–44], and references therein). As the temperature increases, PSD disappears. Previously, we considered PSD in Lennard-Jones and soft-sphere systems [5] and found that the temperature of disappearance of PSD is consistent in both cases with the Frenkel temperature obtained from the VACF and $c_v=2k_B$ criteria. The disappearance of PSD is indeed due to changes in the excitation spectrum, which take place at the Frenkel line [5]. Therefore, it is reasonable to relate the disappearance of PSD to the crossing of the Frenkel line.

To test the presence or absence of PSD, we compute the longitudinal autocorrelation function of the velocity current function:

$$C_L(k,t)=\frac{k^2}{N}<J_z(\mathbf{k},t)\cdot J_z(-\mathbf{k},0)>, \qquad (2)$$

where