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Critical points, phase transitions and water-like anomalies for an isotropic two length scale potential with increasing attractive well

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ABSTRACT

Molecular Dynamic and Monte Carlo studies are performed in a system of particles interacting through core-softened (CS) potential, composed by two length scales: a repulsive shoulder at short distances and the another a variable scale, that can be repulsive or strongly attractive depending on the parameters used. The system show water-like anomalous behavior. The density, diffusion and structural anomalous regions in the pressure versus temperature phase diagram shrink in pressure as the system becomes more attractive. The transition appears with the increase of the attraction well. We found that the liquid–gas phase transition is Ising-like for all the CS potentials and its critical temperature increases with the increase of the attraction. No Ising-like behavior for the liquid–liquid phase transition was detected in the Monte Carlo simulations what might be due to the presence of stable amorphous phases.

1. Introduction

The description of a single component system as particles interacting via a core-softened (CS) two-body potentials has being used as viable strategy to understand the mechanism behind the universal phenomena in anomalous liquids. These potentials exhibit a repulsive core with a softening region with a shoulder or a ramp [1–8]. These models originate from the desire to construct a simple two-body isotropic potential capable of the density [9–11] and diffusion [11–13] anomalies present in water. Another motivation for these studies is the acknowledged possibility that some single component systems display coexistence between two different liquid phases [14,15,14,16–20]. The use of two length scales potentials seems to be an interesting tool for finding the connection between the presence of thermodynamic and dynamic anomalies and the possibility of the presence of two liquid phase.

Complementary to the thermodynamic and dynamic anomalies, water also shows an unusual behavior in its structure. While for normal liquids the system becomes more structured with the increase of the density, water shows a maximum. Such behavior can be characterized by translational order parameter t [21–23] that exhibits a region in which t decreases under compression. The entropy also shows a very peculiar behavior. The excess entropy S_{ex}, defined as the difference between the entropy S of the liquid and the ideal gas, at same density and temperature [24–26,8,27–32], becomes a great tool

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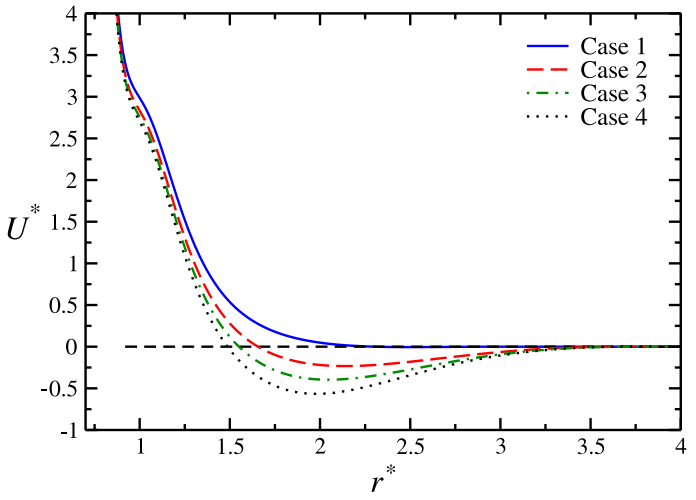

Fig. 1. All the potentials studied here. For the Case 1 there is just a repulsive shoulder at $r^* \sim 1.0$. For the cases 2, 3 and 4 the repulsive shoulder is also maintained at $r^* \sim 1$, but the attractive part is at $r^* = 2.18$, 2.10 and 2.06, respectively. The black dashed line just represent the level zero of potential.

in the investigation of liquid-state anomalies [33]. The region where $(\partial S_{ex}/\partial \rho > 0)$ on isothermal compression corresponds to an anomaly in excess entropy, indicating an existence of distinct forms of local ordering, for a high density limit, where particles are found closer to each other, and a low density region, with large average distance between particles.

The use of core-softened potentials to reveal the origin of these anomalies becomes even more interesting because the anomalies mentioned above are not exclusive of water. Studies have shown that Te [34], Ga, Bi [35], S [36,37], $Ge_{15}Te_{85}$ [38], BeF_2 [39,24,40,41], silica [39,21,24,42] and silicon [43] present water-like anomalies.

The CS potentials show a variety of shapes. They can be ramp-like [44,1,45–49] or continuous shoulder-like [50,5,3,51,8,27,28,52–55,20,56–59]. These work show the presence of the anomalies and only in some cases the existence of the second critical point. The limits in the parameter space that determine the presence of the second critical point is not clear. The presence of an attractive part in the potential is fundamental for the presence of the liquid–liquid phase, but the limit depth for the attractive potential is still not clear.

In this paper we employ a family of CS potentials spanning from purely repulsive to a very attractive case and analyze the behavior of the anomalies, liquid–liquid and liquid–gas critical. Even though this questions was at some extent being explored by ramp-like potentials [51], here we analyze the effect in the anomalies and in the two liquid phases of changing only the energy depth of the attractive part keeping the two length scales fixed.

This paper is organized as follow: in Section 2 we introduce the model; in Section 3 the methods and the simulation details are described; in Section 4 the results are presented; and finally, in Section 5, the conclusions are given.

2. The model

The fluid is modeled by spherical particles with diameter σ and mass m, that interact through a three dimensional two length scales potential given by

$$\frac{U(r_{ij})}{\epsilon} = \epsilon' \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] + \sum_{i=1}^{k} \frac{B_i}{B_i^2 + (r_{ij} - C_i)^2}, \tag{1}$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the distance between two particles i and j. The potential is composed by a standard 12–6 Lennard-Jones (LJ) potential [60] followed by a sum of k Lorentzian distributions centered in C_i and with amplitude $1/B_i$. This composition of the two functions provides a repulsive shoulder at short distances and an attractive global minimum at long distances, depending on the set of parameters used.

The set of parameters were chosen in order to provide different interaction scales. The idea is to have a purely repulsive case in which no liquid–liquid or liquid–gas transitions would be present. In addition, different energy attractive wells were chosen so the liquid–gas and liquid–liquid transitions would appear. The potentials resulting from the choice of the parameters are shown in Fig. 1 The set of parameters that were chosen for each case is shown in Table 1.

Our potential as illustrated in the Fig. 2 was constructed to follow the two length scales Jagla's ramp potential [61] but with an smooth shape. In our parameterization the attractive part of the potential was increased so we can test the effect not only of the continuous forces but also of the depth of the attraction.