

Interplay between structure and density anomaly for an isotropic core-softened ramp-like potential

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Abstract

Using molecular dynamics simulations and integral equations we investigate the structure, the thermodynamics, and the dynamics of a system of particles interacting through a continuous core-softened ramp-like interparticle potential. We found density, dynamic and structural anomalies similar to that found in water. Analysis of the radial distribution function for several temperatures at fixed densities shows a pattern that may be related to the origin of density anomaly.

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1. Introduction

Water is an anomalous substance in many respects. Its specific volume at ambient pressure increases when cooled below $T = 4^\circ\text{C}$. This density anomaly can be well explained by the tetrahedral structure of water, with each molecule forming hydrogen bonds with neighbor molecules. But this is not the only peculiarity of water. While for most materials diffusivity decreases with increasing pressure, liquid water has an opposite behavior in a large region of the pressure–temperature (P–T) phase diagram [1–5]. This diffusivity (or dynamic) anomaly is due to the following mechanism: the increase in pressure disturbs the tetrahedral structure of water by the inclusion of an interstitial fifth molecule that shares an hydrogen bond with another neighbor oxygen. As a result, the bond is weakened and the molecule is free to move. The shared bond breaks and the molecule, by means of a small rotation, connects to another molecule enabling the translational diffusion [3]. The structure and anomalies are therefore deeply related.

The quantification of structure usually employs Errington and Debenedetti's translational order parameter [1] t , that measures the tendency of pairs of molecules to adopt preferential separations, and Steinhardt's [6] orientational order parameter Q_6 . For normal liquids, t and Q_6 increase upon compression, because the system tends to be more structured. For systems with tetragonal symmetry [1] the suitable orientational order parameter is q , that quantifies the extend to which a molecule and its four nearest neighbors assume a

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tetrahedral arrangement. It was found that in SPC/E water both t and q decrease upon compression in a certain region of the P–T phase diagram [1]. This region is referred as the region of structural anomalies.

Is the tetrahedral structure the only one where anomalies would exist? The answer to this question is no. Isotropic models are the simplest framework to understand the physics of liquid state anomalies. A number of such models, in which single component systems of particles interact via core-softened potentials [7] have been proposed. They possess a repulsive core that exhibits a region of softening where the slope changes dramatically. This region can be a shoulder or a ramp. These isotropic models are designed to represent interactions in water and other materials in an effective way.

Recently, we investigated a system of particles interacting through a core-softened, ramp-like potential [8,9] that has density, diffusion, and structural anomalies similar to that found for SPC/E water. In this work, we use the same model to investigate the relation between the local structure of the fluid, as measured by the pair distribution function, and the density anomaly.

2. The results

The model we study consists of a system of N particles of diameter σ , inside a cubic box whose volume is V , resulting in a density number $\rho = N/V$. The interacting effective potential between particles is given by

$$U^*(r) = 4 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + a \exp \left[-\frac{1}{c^2} \left(\frac{r - r_0}{\sigma} \right)^2 \right], \quad (1)$$

where $U^*(r) = U(r)/\varepsilon$. The first term of Eq. (1) is a Lennard-Jones potential of well depth ε and the second term is a Gaussian centered on radius $r = r_0$ with height a and width c . With $a = 5$, $r_0/\sigma = 0.7$ and $c = 1$, this potential has two length scales within a repulsive ramp followed by a very small attractive well, as we can see in Fig. 1. The dimensionless pressure, P^* , temperature, T^* , and density, ρ^* , are given in units of σ^3/ε , k_B/ε , and σ^3 , respectively. Here k_B stands for the Boltzmann constant.

Using integral equation with the Rogers–Young closure [10] to analyze the entire phase diagram, we found a density anomaly for this model [8]. In the neighborhood of the density anomaly region, molecular dynamics simulations were carried out, enabling us to demonstrate that diffusion and structural anomalies are also present in our model [8,9].

The relation between the several anomalies presented for the potential Eq. (1) is shown in Fig. 7 of Ref. [9]. We found that the region of density anomaly is located entirely inside the region of diffusion anomalies, which in its turn is inside the region of structural anomalies. These hierarchy of anomalies is the same as the one found for the SPC/E water (compare Fig. 7 of Ref. [9] and Fig. 4 of Ref. [1]).

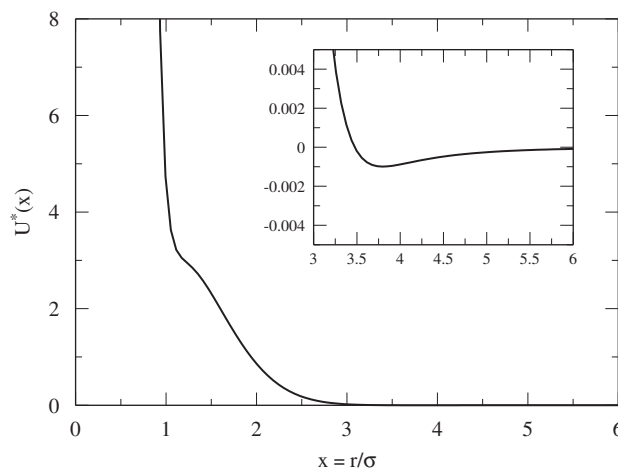


Fig. 1. Interaction potential from Eq. (1) with parameters $a = 5$, $r_0/\sigma = 0.7$ and $c = 1$, in reduced units. The inset shows a zoom in the very small attractive part of the potential.

In order to understand the relation between structure and density anomaly, we analyze the pair distribution functions of our model (Fig. 2). We see clearly three well defined regimes, namely:

- (i) For low densities, below the region where density anomaly occurs (see Fig. 3), the remarkable point is that the first peak (close to the core) of the $g(r)$ is very small, and the population of particles at this distance is negligible. Note the arrows indicating the direction of temperature increase.
- (ii) For intermediate densities, inside the region of density anomaly, we can see a considerable increase of the first peak of the $g(r)$ compared to the low density regime. This increase is more pronounced at low temperatures: for temperatures $T^* = 0.15, 0.18,$ and 0.23 , just inside the density anomaly domain (see the TMD line in Fig. 3). Analyzing the first peak of $g(r)$, the first curve from bottom to top corresponds to the lowest temperature. In the second peak of the $g(r)$, close to 2.5σ , there is an opposite behavior: the lowest

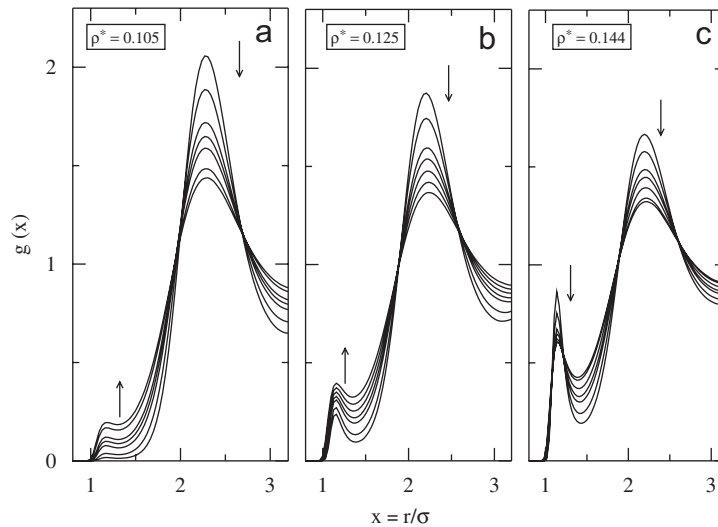


Fig. 2. Pair distribution functions for three densities and seven temperatures of our model Eq. (1). The densities are the same as those illustrated in Fig. 3. The arrows point to increasing temperatures: $T^* = 0.15, 0.18, 0.23, 0.262, 0.3, 0.35,$ and 0.4 , similar to the arrows in Fig. 3.

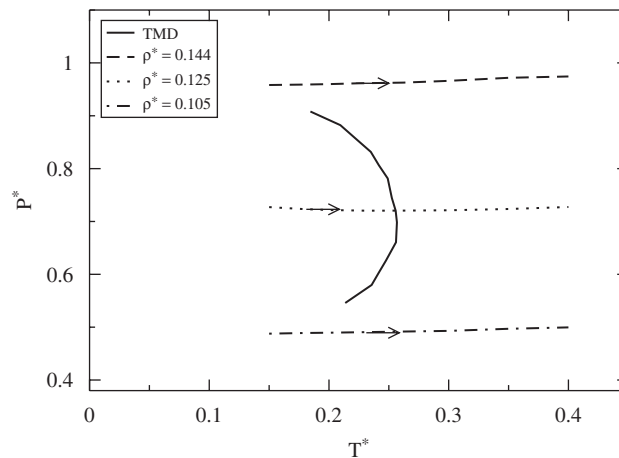


Fig. 3. Pressure–temperature phase diagram for the model Eq. (1). The three isochores shown in this figure correspond to the regions below, inside, and above the region where density anomaly occurs.

temperature corresponds to the first curve from top to bottom, and the arrow points downwards to higher temperatures.

- (iii) For a high density, above the density anomaly region, the interesting thing to note is the inversion of the trend in the first peak of $g(r)$. Close to the core, the lowest temperature has the highest first peak. The trend in the second peak remains unchanged.

This analysis suggests that the behavior of the $g(r)$ underlies the density anomaly effect in a close way. The anomaly develops when the inner peak, close to core distances, becomes increasingly important. We see that the first peak of the $g(r)$ tends to increase faster for low temperatures upon compression than for the high temperatures. This suggests a connection between density anomaly and structure depending on the derivative of the $g(r \approx \sigma)$ with respect to the temperature at fixed density. A similar study of $g(r)$ for several densities at constant temperature was also applied to show its pattern related to the structural anomaly region [9].

3. Conclusions

Using molecular dynamic simulations we have studied the density behavior, the diffusivity, and the structure of fluids interacting via a three-dimensional continuous core-softened potential with a continuous force. Our model exhibits a region of density anomaly, inside which the density increases as the system is heated at constant pressure, and a region of diffusion anomaly, where the diffusivity increases with increasing density [8]. In the pressure–temperature phase diagram, the density anomaly region lies inside the region of diffusion anomaly. Complementary to the thermodynamic and dynamic anomalies, both t and Q_6 behave anomalously in a large region of the temperature–density plane.

This continuous core-softened pair potential, despite not having long-ranged or directional interactions, exhibits thermodynamic, dynamic [8], and structural anomalies [9] similar to the ones observed in SPC/E water [1,2]. Therefore, the presence of anisotropy in the interaction potential is not a requirement for the presence of thermodynamic, dynamic, and structural anomalies.

We also found that the pattern of isochoric change of the pair distribution function $g(r)$ with temperature is closely related to the presence of density anomaly. The inset of this anomaly may be related to the derivative of population of molecules with respect to the temperature in a distance corresponding to the core distance.

Acknowledgments

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