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Dynamic anomalies of fluids with isotropic doubled-ranged potential

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Abstract

Using molecular dynamics simulations we investigate the ability of an analytical three-dimensional double well in reproducing dynamic anomalies found experimentally and by computational models in liquid water. We find anomalous behavior in the stable region of the phase diagram if the outer minimum is deeper than the inner minimum. In the case of a deeper inner minimum, anomalous behavior is also present but inside the unstable region.

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1. Introduction

The prediction of structural, dynamic and thermodynamic properties and the phase behavior of fluids based solely on the shape of the intermolecular interaction potential is an important goal in the study of liquids and in the understanding of the peculiarities

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of the liquid state. The simplicity of this surmise has not only theoretical interest but also practical consequences [1]. In spite of these motivations and precepts of developing a much better molecular-level picture of the liquid matter, this goal is far from being achieved. Although for some simple potential the use of integral equations in the form of hypernetted-chain approximation can give an estimate of the phase stability [2], the mathematical complexity of the interaction potentials used even for simple liquid does not allow an analytical approach. Despite of this, some progress can be made choosing only liquids that share the same type of structure, for instance, a tetrahedrical local structure. The most familiar tetrahedral liquid is water not only due to its abundance but also because of the occurrence of some remarkable features such as the presence of structural, dynamic or thermodynamic anomalies. The question is to determine which characteristics of the intermolecular interaction potential would be needed to induce anomalies in the liquid phase behavior of fluids governed by this potential. One of the most familiar mysteries in water's behavior is the density anomaly: at sufficient low temperatures, warming the liquid causes it to shrink. There is an increasing awareness that including this one property in the potential will reveal the origins of the others.

Recently, following an earlier hypothesis of Kamb [3], and supported by experimental results [4–6] it has been shown that the increase in density on melting is related to a distortion in the non-nearest-neighbor coordination, i.e., bending of hydrogen bonds. The key point is therefore modeling the behavior of the system based not on a potential mimicking the first neighbors interactions, as in mostly current models, but on a potential capability in describing the peculiar interactions between second neighbors [7,8]. These interactions are double-ranged: the competition between two scales is responsible for many of the anomalies of water. In this spirit one can understand the success of a simple model as the core-softened potential introduced by Stell et al. [9]. It was shown that a one-dimensional hard-core system showing a first-order phase transition could be capable of exhibiting two (or even three) phase transitions if the hard-core is softened in a reasonable way. It is, however, not clear if the same essential features of this model would produce anomalies in three-dimensional systems.

Another example is the double-well Takahashi model [7], with an inner shallow well and a outer deeper well. This model exhibits a density maximum in one-dimensional systems, with the correct pressure dependence: this density maximum becomes broader and shifts to lower temperatures by increasing the pressure. This approach, however, seems not to work in three-dimensional systems [8,10] and the question was posed if the three-dimensional potential, besides being double-ranged, also must have an angular dependence in order to show anomalies. Cho and co-workers [11] also proposed an analytic double-well potential without angular dependence, with a slight modification on a Lennard–Jones potential, adding a Gaussian-shaped perturbation. This potential seems to have anomaly in the density. However, a more consistent exploration of the parameter space is necessary in order to determine if this is the case for all range of parameters. Later, Cho et al. [12] argued that only non-local potentials could reproduce all water's anomalies. Within their analysis the potential should have a strong angular dependence and favor the build-up of a second-neighbor structure [13].

Following a similar approach as the original Takahashi model, Jagla showed [14] that several anomalies could be described by a simple interaction potential with two

competing equilibrium distances. The model including a global term for attractions displays a liquid phase with a first-order line of liquid–gas transition ending in a critical point. This potential, however, is difficult to implement in a molecular dynamics simulation, because the attraction term is not explicitly taken into account and the system needs long equilibration times. Besides the three models mentioned above, a number of lattice [15] and continuous [16] core-softened potentials has been proposed.

However, besides the thermodynamic, water also has dynamic anomalies. While for most materials diffusivity decreases with pressure, liquid water has an opposite behavior in a large region of the phase diagram [17–22]. A good model for water and tetrahedral liquids should not only exhibit the thermodynamic but also the anomaly in the mobility. These dynamical anomalies are related to the competition between the local tetrahedral structure of first neighbors—which tends to decrease the mobility and the distortion of the structure of first and second neighbors, with weakened hydrogen bonds and interstitial water molecules—which tends to increase the mobility. This anomaly in the diffusivity is enhanced at low temperatures where the two scales phenomena becomes more prominent. In the present paper, we check if a simple model in which the particles are model as modified soft spheres interacting with two competing ranges exhibits the anomalies present in water. Particularly we study the diffusivity of two model cases: one in which the outer minimum is deeper and another in which the inner minimum is deeper. This paper is organized as follows. In the next section the model and methods are described and in Section 3 the results and the conclusions are shown.

2. The model and the methods

Our model system consists of softened spheres with an intermolecular potential displaying a repulsive short-ranged component showing r^{-12} dependence and a double-ranged attractive component, by adding a Gaussian to a normal Lennard–Jones potential [11], as follows:

$$U = 4[r^{-12} - r^{-6}] + \alpha \exp\left(-\frac{(r-\beta)^2}{\gamma^2}\right) . \tag{1}$$

This potential can represent a whole family of intermolecular interactions, from weak repulsive shoulder to deep double well potentials, depending on the choice of the values of α, β and γ. Fig 1 show two choices of parameters that illustrate two significative cases: one in which the outer minimum is deeper and another in which the inner minimum is minimum. Depending on the choice of parameters, we can obtain either a potential similar to the one employed by Cho [7] or the one introduced by Jagla [14].

We carried out molecular dynamics simulations in the microcanonical ensemble of 256 particules interacting with an intermolecular potential given by Eq. (1). A broad range of thermodynamic conditions, expressed as several densities and temperatures was chosen to explore the phase diagram of the fluid described by this potential. Using reduced units for density $\rho^* = \rho\sigma^3$, for temperature $T^* = Tk_B\varepsilon^{-1}$, the values for ρ^* and T^* were 0.60–1.00 and 0.30–1.00, respectively. Thermodynamic parameters

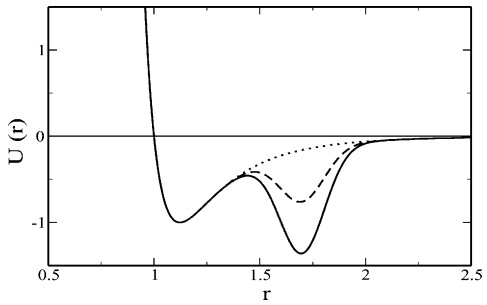

Fig. 1. Model potential I (solid line) with an outer deeper minimum and parameters $\alpha=-1.2$, $\beta=1.7$, $\gamma=0.15$, model potential II (dashed line) with an inner deeper minimum, and parameters $\alpha=-0.6$, $\beta=1.7$, $\gamma=0.15$, compared with a normal Lennard–Jones potential (dotted line).

(internal energy and pressure) were calculated over 3,000,000 step long simulations. Analysis of the dependence of the pressure against density along isotherms, aided by visual inspection of the final structure allows to check if the system is unstable or not. We measure the mean-square displacement averaged over different initial times $\langle \Delta r^2(t) \rangle = \langle [r(t+t_0) - r(t)]^2 \rangle$ and then the diffusion constant is calculated using the relation $D = \langle \Delta r^2(t) \rangle / 6t$.

3. Results and conclusions

The diffusion constant is calculated for two types of potentials: (I) $\alpha=-1.2$, $\beta=1.7$ and $\gamma=0.15$, (II) $\alpha=-0.6$, $\beta=1.7$ and $\gamma=0.15$. Potential I exhibit a competition between a first attractive shell and a second deeper minimum. This competing interactions can generate two liquid phases with different densities [11,15,16] and a resulting density anomaly. The mobility of potential I, illustrated in Fig. 2, is similar to the behavior we found [22] in SPCE [23] supercooled water. The error in the values of the diffusion constant are about 1% for low densities where the anomaly occurs. The diffusivity increases as the density is lowered, reaches a maximum and decreases. It is not clear if for this potential the diffusivity increases at very low densities [22] because the system cavitates before this happens. Potential II has a competition between a deeper inner well and an shallow outer shell. This competition can also generate two liquid phases with different densities [15] and a resulting density anomaly. The diffusion constant related to Potential II, illustrated in Fig. 3, is also anomalous, however its anomalous behavior occurs inside the unstable region where the system already is phase separated.

According Cho et al. [7,16] a double well Takahashi model would exhibit a density maximum only if the outer well is deeper than the inner well. Although our potential is not of a Takahashi type, its shape roughly resembles that potential by an adequate choice of parameters. Our main conclusion is that even if the outer well is shallower than the inner well the anomalies are still present, however they are covered by the phase separation. A systematic study in progress of the dependence of the fluid

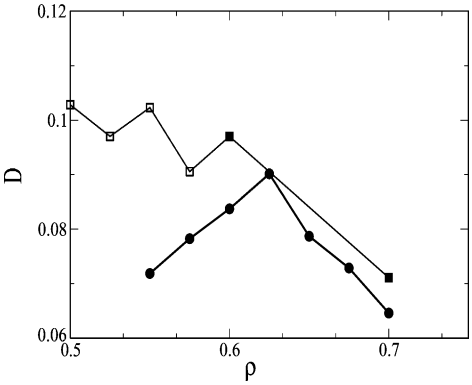

Fig. 2. Diffusion coefficient as a function of density for temperatures $T=0.70$ (circles) and $T=0.75$ (squares) using Potential I. All quantities are in reduced units. Open symbols correspond to systems where there is cavitation.

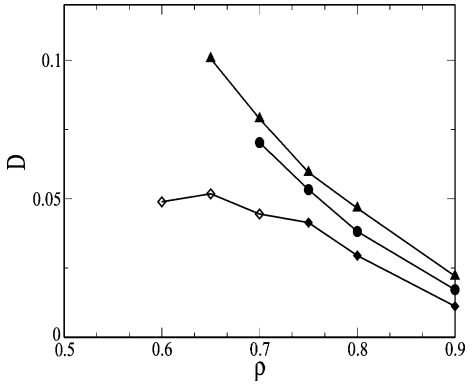

Fig. 3. Diffusion coefficient as a function of density for temperatures $T=0.60$ (diamonds), $T=0.70$ (circles) and $T=0.80$ (triangles), using Potential II, same conventions as Fig. 2.

behavior with the choice of parameters will enable us to better understand the hierarchy of the several anomalies in such a two-ranged analytic model.

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