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Phase diagram and thermodynamic and dynamic anomalies in a pure repulsive model

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HIGHLIGHTS

- We show that a pure repulsive interaction potential exhibits density anomaly.
- The dynamics shows an increase in diffusion coefficient with the increase of pressure.
- A fragile-to-strong transition is only observed in the vicinity of the critical line if there is a change of structure.

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ABSTRACT

Using Monte Carlo simulations a lattice gas model with only repulsive interactions was checked for the presence of anomalies. We show that this system exhibits the density (temperature of maximum density—TMD) and diffusion anomalies as present in liquid water. These anomalous behaviors exist in the region of the chemical potential *vs* temperature phase diagram where two structured phases are present. A fragile-to-strong dynamic transition is also observed in the vicinity of the TMD line.

1. Introduction

Water is one of the most important liquids in the world. Its relevance to life and to the industrial processes are a consequence of many of its anomalous properties. One example is the density anomaly. While for most liquids density decreases monotonically as temperature increases at constant pressure, this is not the case of liquid water. For high temperatures the density decreases with the increase of temperature, but at approximately 4 °C at 1 atm density reaches a maximum and decreases monotonically [1]. This water property is responsible for keeping the water liquid inside lakes and rivers at subzero temperatures while the surface is frozen. This is one of the 70 known water anomalous properties [2]. Another peculiar water behavior is that it can diffuse faster in a more dense state. For normal liquids we expect that the diffusion coefficient, D, at constant temperature increases with the decrease of pressure, since mobility is enhanced in a less dense medium. However, for water there is a range of pressures in which diffusion exhibits a non monotonic behavior with pressure and it increases as water gets more dense [3].

The diffusion coefficient of water exhibits another anomalous behavior: it changes from a non-Arrhenius diffusion to an Arrhenius diffusion when temperature is decreased at constant pressure in the region of pressure *vs* temperature phase diagram where the response functions have a large increase. Water is fragile (non-Arrhenius) at the room and moderately supercooled temperatures [4], but it has been shown to be a strong liquid (with Arrhenius behavior) by dielectric relaxation

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measurements near the glass transition temperature [5] for confined water. Experiments using NMR and quasi-elastic neutron scattering [6] and with nuclear magnetic resonance [7] confirm the fragile-to-strong transition in the "no-man's land". This is the region of the pressure *vs* temperature phase diagram where no liquid phase is found since homogeneous nucleation takes place. However, crystallization can be avoided in confined systems. Recently, the existence of a fragile-to-strong transition is associated with the presence of a liquid–liquid transition as follows. Experiments and simulations show that a fragile-to-strong transition occurs when the continuation of the liquid–liquid phase transition, the so called Widom line, is crossed at constant pressure [8].

Water can form hydrogen bonds and this interaction between molecules has been considered as the main mechanism for anomalies [9]. Due to the hydrogen bonds water molecules organize themselves into arrangements of four bonded molecules, the tetramers. They can form two types of structures, one more rigid and open in which all molecules are bonded and another more malleable and close in which only part of the molecules are bonded. These two structures are present in the formation of hydrogen bond network in percentages that vary. While the open structure occupies less volume and requires less pressure, the closed structure has lower energy. This competition is responsible for the density and diffusion anomaly [10–13] and for the reentrant multiple solid phases [14,15].

Recognizing that the competition between two structures is related to the mechanism for the presence of anomalies, a number of effective two length scales models have been proposed [14,16–25]. The simplest version of these models is based on the lattice gas structure [26–30]. In these cases the directionality of the hydrogen bonds is incorporated to the occupation variable with the addition of an arm variable [30,19,31] and in some cases with the ad hoc increase of volume when the arm values are ordered [17]. Recently a couple of lattice models have been proposed in which no arm variable is presented. Instead of the directionality the anomalies of water are obtained by the competition between two length scales: one attractive and one repulsive [32,33]. In both models the presence of attraction is fundamental for the existence of anomalies.

The existence of density and diffusion anomalies in lattice models with no directionality indicates that the anisotropy in this system is not fundamental for the existence of these anomalies. Then the question arises if the attractive interaction is relevant or not for a system to exhibit anomalies. In order to answer to this question, in this paper we study the phase diagram of a triangular lattice gas model that presents only repulsive interactions: an infinity repulsive hard-core interaction with the nearest neighbors and a finite repulsive interaction with the next to nearest neighbors. Our basic assumption is that these two repulsive length scales can reproduce a competition between two ordered structures as presented in water, that we believe is responsible for the anomalies. Hence, we test if this model exhibits the density and diffusion anomalies. In addition we also verify if in the vicinity of the anomalous region multiple liquid phases are presented. Finally we also verify if the criticality is followed by a dynamical fragile-to-strong transition, particularly in the vicinity of the diffusion anomalous region in the chemical potential *vs* temperature phase diagram.

This article is divided in sections as follows. In Section 2 we present the model, in Section 3 the Monte Carlo simulations are described. In Section 4 results are shown and conclusions are presented in Section 5.

2. The model

We considered a two dimensional triangular lattice gas model with L^2 sites. Each lattice site thus can be empty or occupied by a particle, has six nearest neighbors with a distance a and six next to nearest neighbors with distance $\sqrt{3}a$ where a is the length scale of the model. The particles interact by a two-scale repulsive potential: an infinite repulsive hard core interaction with its nearest neighbors and a finite repulsive interaction ϵ with its next to nearest neighbors. Therefore, if a site is occupied, its six nearest neighbors must be all empty and this particle will interact with its six next to nearest neighbors if they are occupied too [34]. Thus, the Hamiltonian for this model can be written as:

$$\tilde{\mathcal{H}} = \frac{1}{2}\sum_{i=1}^{L^2}\sum_{\langle i,j\rangle} n_i n_j \epsilon_{ij} \tag{1}$$

where $\langle i, j\rangle$ indicates the interaction of next to nearest neighbor pairs of sites. If a site i is empty $n_i = 0$, and if it is occupied: $n_i = 1$ and $\epsilon_{ij} = \infty$ for nearest neighbors and $\epsilon_{ij} > 0$ for the next to nearest neighbors. In the Grand Canonical Ensemble, we can write an effective Hamiltonian, namely

$$\mathcal{H} = \sum_{\langle i,j\rangle}^{L^2} \epsilon_{ij} n_i n_j - \mu \sum_{i=1}^{L^2} n_i. \tag{2}$$

And the Grand Potential will be defined as:

$$\Phi(T, \mu) = \langle \mathcal{H}\rangle - TS. \tag{3}$$

This model was originally proposed by Almarza et al. [34] and the full phase diagram was obtained by an improved mean field approach and simulations.