Diffusion Anomaly
in a three dimensional lattice gas

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Abstract

We investigate the relation between thermodynamic and dynamic properties of
an associating lattice gas (ALG) model. The ALG combines a three dimensional
lattice gas with particles interacting through a soft core potential and orientational
degrees of freedom. From the competition between the directional attractive forces
and the soft core potential results two liquid phases, double criticality and density
anomaly. We study the mobility of the molecules in this model by calculating the
diffusion constant at a constant temperature, D. We show that D has a maximum
at a density ρ_{max} and a minimum at a density $\rho_{min} < \rho_{max}$. Between these densities
the diffusivity differs from the one expected for normal liquids. We also show that in
the pressure-temperature phase-diagram the line of extrema in diffusivity is close to
the liquid-liquid critical point and it is partially inside the temperature of maximum
density (TMD) line.

1 Introduction

Most liquids contract upon cooling. This is not the case of water, a liquid where
the specific volume at ambient pressure starts to increase when cooled below

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$T = 4^oC$ at atmospheric pressure [1]. This effect is called density anomaly. Besides the density anomaly, there are sixty-two other anomalies known for water.[2] The diffusivity is one of them. For normal liquids the diffusion coefficient, D, decreases under compression. However, experimental results have show that for water at temperatures approximately below 10^oC, the diffusion coefficient increases under compression and has a maximum (square symbols in Fig. 1). For temperatures above 10 ^oC, D behaves as in a normal liquid. The temperature of maximum density (TMD) line (circles in Fig. 2), inside which the density anomaly occurs, and the line of maximum in diffusivity are located in the same region of the pressure-temperature (P-T) phase diagram of water. [3] Simulations also show thermodynamic and dynamic anomalies. The simple point charged/extended (SPC/E) model for water exhibits in the P-T phase diagram a TMD line. The diffusion coefficient has a maximum and a minimum that define two lines at the P-T phase diagram, the lines of maximum and minimum in the diffusivity coefficient. [4–6] The TMD and the lines of maximum and minimum in the diffusion are located at the same region at the P-T phase diagram for the SPC/E model (see Fig. 1). Errington and Debenedetti [5] and Netz *et al.*[4] found, in SPC/E water, that there exists a hierarchy between the density and diffusion anomalies as follows. The diffusion anomaly region, inside which the mobility of particles grow as the density is increased, englobes the density anomaly region, inside which the system expands upon cooling at constant pressure(see Fig. 1) . Experiments for real water support these simulational results (see Fig. 2). [3]

It was proposed a few years ago that these anomalies are related to a second critical point between two liquid phases, a low density liquid (LDL) and a high density liquid (HDL) [7]. This critical point was discovered by computer simulations. This work suggests that the critical point is located at the supercooled region beyond the line of homogeneous nucleation and thus cannot be experimentally measured. In spite of this limitation, this hypothesis has been supported by indirect experimental results [8,9].

One question that arises in this context is what kind of potential would be appropriated for describing the tetrahedrally bonded molecular liquids, capturing the presence of thermodynamic anomalies? Realistic simulations of water [10–12] have achieved a good accuracy in describing the thermodynamic and dynamic anomalies of water. However, due to the high number of microscopic details taken into account in these models, it becomes difficult to discriminate what is essential to explain the anomalies. On the other extreme, a number of isotropic models were proposed as the simplest framework to understand the physics of the liquid-liquid phase transition and liquid state anomalies. From the desire of constructing a simple two-body isotropic potential capable of describing the complicated behavior present in water-like molecules, a number of models in which single component systems of particles interact via core-softened (CS) potentials have been proposed. They possess a repulsive

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core that exhibits a region of softening where the slope changes dramatically. This region can be a shoulder or a ramp [13–32]. Unfortunately, these models, even when successful in showing density anomaly and two liquid phases, fail in providing the connection between the isotropic effective potential and the realistic potential of water.

It would, therefore, be desirable to have a theoretical framework which retains the simplicity of the core-softened potentials but accommodates the tetrahedral structure and the role played by the hydrogen bonds present in water. A number of lattice models in which the tetrahedral structure and the hydrogen bonds are present have been studied [33–44]. One of them, is the three-dimensional model proposed by Roberts and Debenedetti [35–37] and further studied by Pretti and Buzano [40] defined on the body centered cubic lattice. According to their approach, the energy between two bonded molecules rises when a third particle is introduced on a site neighbor to the bond. Using a cluster mean-field approximation and computer simulations they were able to find the density anomaly and two liquid phases. In this case, the coexistence between two liquid phases may arise from the competition between occupational and Potts variables introduced through a dependency of bond strength on local density states.

Recently we have proposed an associating lattice-gas (ALG) model which retains the simplicity of the core-softened potentials but accommodates the tetrahedral structure and the role played by the hydrogen bonds present in water. This model system is a lattice gas with ice variables [45] which allows for a low density ordered structure. Competition between the filling up of the lattice and the formation of an open four-bonded orientational structure is naturally introduced in terms of the ice bonding variables, and no *ad hoc* introduction of density or bond strength variations is needed. In that sense, our approach bares some resemblance to that of continuous softened-core models [46–48]. Studying this simple model in two and three dimensions we were able to find two liquid phases, two critical points and the density anomaly [23][24][49][50].

In this paper, in the framework of the ALG, we address two questions: (i) is the presence of diffusion anomaly related to the presence of density anomaly? (ii) if so, what is the hierarchy between the two anomalies and the presence of a second critical point? We show that the two anomalies are located in the same region of the P-T phase diagram, close to the second critical point and that the region on the P-T phase diagram in which the density anomaly is present encloses the region in which the diffusion anomaly exists.

In sec. II the model is introduced and the simulation details are given. Sec. III is devoted to the main results and conclusion ends this session.
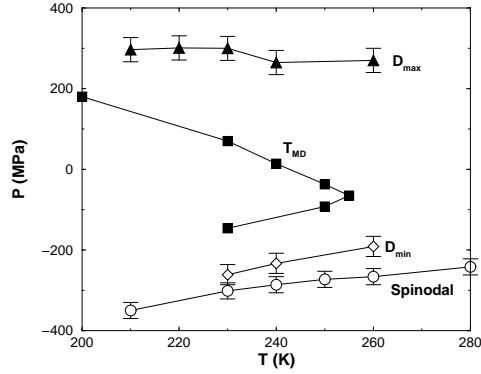
Fig. 1. Simulation data for SPC/E water from the work of Netz *et al.*.[4] The triangles determine the loci where the diffusion has a local maximum value with increasing density at fixed temperature, and the diamonds mark its local minima. The squares determine the temperature of maximum density line, where density anomaly occurs, and the circles locate the liquid-gas spinodal.
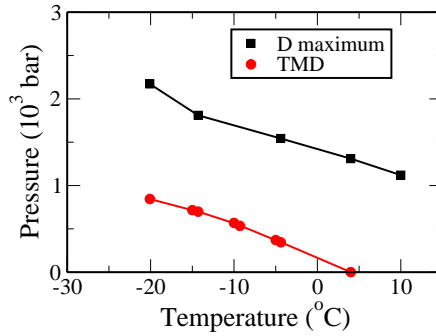

Fig. 2. Experimental data for water extracted from the work of Angell *et al.*.[3] The squares determine the loci where the diffusion has a maximum value with increasing pressure at fixed temperature. The circles stands for the temperature of maximum density (TMD) line, location where density anomaly occurs.
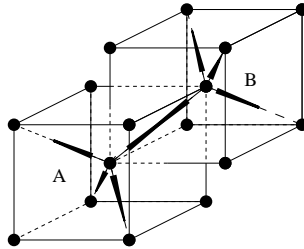

Fig. 3. The model.

2   The Model

Recently [49], we have considered a body-centered cubic lattice with V sites, where each site can be either empty or filled by a water molecule. Associated to each site there are two kinds of variables: an occupational variables, n_i, and an orientational one, τ_i^{ij}. For $n_i = 0$ the i site is empty, and $n_i = 1$

represents an occupied site. The orientational state of particle i is defined by the configuration of its bonding and non-bonding arms, as illustrated in Fig. (3). Four of them are the usual ice bonding arms with $\tau_i^{ij} = 1$ distributed in a tetrahedral arrangement, and four additional arms are taken as inert or non-bonding ($\tau_i^{ij} = 0$). Therefore, each molecule can be in one of two possible states A and B as illustrated in Fig. (3). A potential energy ε is associated to any pair of occupied nearest-neighbor (NN) sites, mimicking the van der Waals potential. Here, water molecules have four indistinguishable arms that can form hydrogen-bonds (HB). An HB is formed when two arms of NN molecules are pointing to each other with $\tau_i^{ij} = 1$. An energy γ is assigned to each formed HB.

In resume the total energy of the system is given by:

$$E = \sum_{(i,j)} n_i n_j \left(\varepsilon + \gamma \tau_i^{ij} \tau_j^{ji} \right) \ . \tag{1}$$

The interaction parameters were chosen to be $\varepsilon > 0$ and $\gamma < 0$, which implies in an energetic penalty on neighbors that do not form HBs. From this condition results the presence of two liquid phases and the density anomaly.

For studying the mobility, we have performed Monte Carlo simulations of a system of N particles interacting as specified by the Hamiltonian of Eq.(1). The procedure for computing the diffusion coefficient goes as follows. The system is equilibrated at a fixed chemical potential and temperature. In equilibrium this system has n particles. Starting from this equilibrium configuration at a time $t = 0$, each one of these N particles is allowed to move to an empty neighbor site randomly chosen. The move is accepted if the total energy of the system is reduced by the move, otherwise it is accepted with a probability $\exp(\Delta E / k_B T)$ where ΔE is the difference between the energy of the system after and before the move. After repeating this procedure Nt times, the mean square displacement per particle at a time t is computed and the diffusion coefficient is obtained from

$$\overline{D} = \lim_{t \to \infty} \frac{\langle \Delta \overline{r}(t)^2 \rangle}{6 \overline{t}} \ . \tag{2}$$

where $\overline{r} = r/a$ and a is the distance between two neighbor sites and $\overline{t} = t/t_{MC}$ is the time in Monte Carlo steps.
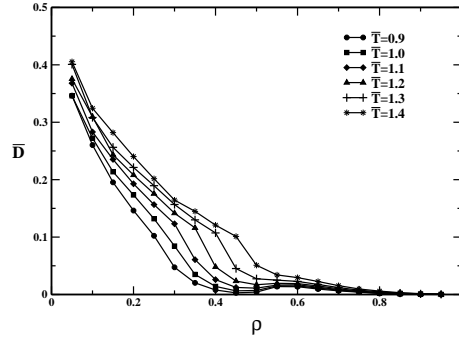
Fig. 4. Reduced Diffusion coefficient vs. density for $\overline{T} = 0.9, 1.1, 1.2, 1.3, 1.4$. $\overline{D}$
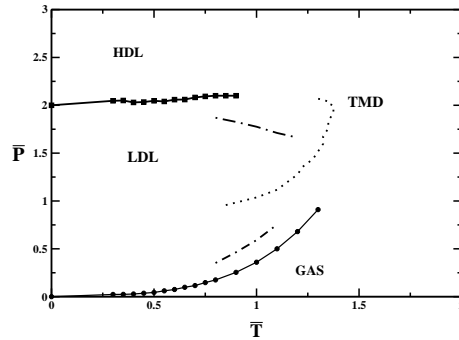

Fig. 5. Reduced pressure vs. reduced temperature phase diagram showing the the two liquid phase, two critical points, the density anomaly (the TMD is the dotted line) and the diffusion anomaly regions (the temperature of maximum diffusion is the upper dot-dashed line and the temperature of minimum diffusivity is the lowe dot-dashed line).

3 Results and Conclusions

In order to find if the three-dimensional associating lattice gas exhibits diffusion anomalies, we have analyzed how $\overline{D}$ varies with the number density $\rho = N/(2L^3)$ for a fixed temperature. Fig. (4)illustrates the behavior of $\overline{D} = D\tau_{MC}/a^2$ for $\overline{T} = k_B T/\varepsilon = 0.9, 1.1, 1.2, 1.3, 1.4$ where a is the lattice distance and τ_{MC} is the tipical Monte Carlo time step. For high temperatures, $\overline{T} > 1.2$, the diffusion increases with decreasing density as in a normal liquid.

A different scenary appears for lower temperatures. The reduced diffusion coefficient, $\overline{D}$ still decreases as ρ increases for very low densitie. However, as the density is increased $\overline{D}$ has a minimum at ρ_{Dmin}, and increases with the increase of density from $\rho_{D_{min}} < \rho < \rho_{D_{max}}$. Increasing the density above ρ_{Dmax}, $\overline{D}$ decreases again as expected. Therefore, there is a region of densities $\rho_{Dmax} > \rho > \rho_{Dmin}$ where the diffusion coefficient is anomalous, increasing with density. This behavior is similar to the diffusion anomaly present in SPC/E water. A diffusion anomaly in the ALG model is observed in the range of temperatures $0.75 < \overline{T} < 1.2$ illustrated in Fig. (5). The region in the $\overline{P}$

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$-\overline{T}$ plane (where ($\overline{P} = P/\varepsilon/a^3$) where there is an anomalous behavior in the diffusion is bounded by ($T_{D\min}, P_{D\min}$) (lower line)and ($T_{D\max}, P_{D\max}$) (upper line) and lies partially inside the region of density anomalies what differs from the behavior observed experimentally and in SPC/E water (see Fig. (1) and Fig. (2)) but coincides with the behavior shown for non smooth ramp-like potentials [51] that might be relevant for other tetrahedral materials.

In resume we have shown that the presence of a density anomaly seems to be associated with the presence of diffusion anomaly, confirming observations made in other models [22,30] and in water [4,52,53]. This seems to indicate that as the particles gain more energy by being close together, this gain facilitates the mobility. The hierarchy between the anomalies resembles the one observed in the purely repulsive ramp-like discretized potential [51]. The link between the two models is the presence of two competing interaction distances and the non smooth transition between them. The first ingredient seems to be the one that defines the presence of the anomalies, while the second might govern the hierarchy between them [51][22][30]. Similar behavior should be expected in other models where the density anomaly is also present [54]-[32]

Acknowledgments

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