



Waterlike features, liquid–crystal phase and self-assembly in Janus dumbbells



José Rafael Bordin

1-Campus Caçapava do Sul, Universidade Federal do Pampa, Av. Pedro Anunciação, 111, CEP 96570-000, Caçapava do Sul, RS, Brazil

HIGHLIGHTS

- Molecular dynamics simulations of Janus nanoparticles.
- The monomeric system do not have anomalies, but density and diffusion anomalies were observed for the Janus dumbbells.
- Distinct self-assembled structures obtained depending on density and temperature.
- Liquid–crystal phase.

ARTICLE INFO

Article history:

Received 29 January 2016

Received in revised form 24 March 2016

Available online 27 April 2016

Keywords:

Waterlike anomalies

Anomalous fluids

Janus dumbbells

Self-assembly

ABSTRACT

We explore the phase diagram of Janus nanoparticles using Molecular Dynamics simulations. Each monomer in the dimer has distinct characteristics. One type of monomer interacts by a Lennard Jones potential, while the other type interacts through a two length scale potential. Previous studies for the monomeric system using this specific two length scale potential do not indicate the presence of waterlike anomalies. However, our results show that the combination of two length scales potential and LJ potential in the Janus nanoparticle will lead to thermodynamic and dynamic anomalies. The self-assembly properties were also explored. We observe distinct kinds of self-assembled structures and a liquid–crystal phase. This result indicates that it is possible to create Janus nanoparticles with waterlike features using monomers without anomalous behavior. The anomalies and structures are explained with the two length scale potential characteristics.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Most part of the materials contract on cooling at constant pressure. Also, is expect a decrement in the diffusion coefficient when the pressure of the system is increased. However, this is not the case from the so called anomalous fluids. The most well known anomalous fluid is water [1,2], with 73 known anomalies [3]. Liquid water at 1.0 atm have a maximum in the density at the temperature of 4 °C, expanding as is cooled down to 0 °C. Other materials, such as silicon [4], silica [5], Te [6], Bi [7], Si [8], $\text{Ge}_{15}\text{Te}_{85}$ [9], liquid metals [10], graphite [11] and BeF_2 [12], also present thermodynamic anomalies. Water [13], silicon [14] and silica [4] show diffusion anomaly, characterized by a maximum in the diffusion coefficient at a constant temperature.

Core-softened (CS) potentials with two length scales (TLS) have been widely used to study the general properties and characteristics of fluids with anomalous behavior [15–18]. TLS potentials are characterized by having two preferred particle–particle separations, while one length scale (OLS) potential, as the Lennard Jones (LJ) potential, shows only one characteristic distance.

E-mail address: josebordin@unipampa.edu.br.

<http://dx.doi.org/10.1016/j.physa.2016.04.032>

0378-4371/© 2016 Elsevier B.V. All rights reserved.

TLS potentials are able to reproduce waterlike anomalies in qualitative way if competition exists between the two characteristic distances [17,19,20]. If the energy penalty to the particle moves from one scale to another is higher than the particle kinetic energy, then the particle will get trapped in one length scale, and there will be no competition. As a consequence, there will be no anomalous behavior.

Another system of interest is colloidal suspensions. Despite the fact that anomalous properties were not observed for this colloidal system, experiments [21,22] show that the effective interaction between the colloids has a TLS shape. Therefore, they can be studied using a TLS potential without competition between the scales.

Particularly, colloidal Janus nanoparticles have attracted the attention of scientists due to the large range of applications of these new materials, including medicine, catalysis, photonic crystals, stable emulsions, biomolecules and self-healing materials [23–28]. Dumbbells colloids are formed by two spheres that overlap with a separation that varies from an almost total overlap to one or two monomer diameters. The molecule anisotropy plays quite a relevant role. The properties of the system depend on the interaction potential that varies with their spatial separation and their relative orientations. In the case of Janus dumbbells [29–32], each monomer has distinct characteristics, as charged/neutral or hydrophilic/hydrophobic. The competition between attractive and repulsive forces leads to the formation of self-assembly lamellae or micellae phases [33–38].

Recently, the production of silver–silicon (Ag–Si) [30], silica–polystyrene (SiO₂–PS) [39] and tantalum silicide–silicon (TaSi₂/Si) [40] hybrid Janus dimers were reported. Silicon and silica are classified as anomalous fluids, and the silicon–silicon or silica–silica interaction in the pure system can be modeled by a TLS potential with competition between the scales. The other monomers can be described by an one length scale potential and consequently does not show the presence of the waterlike thermodynamic and dynamic anomalies. In our previous work, we have shown that if the TLS potential shows dynamical and thermodynamical anomalous behavior for the monomeric case, the Janus dimer will have anomalies accordingly with the non-anomalous monomer properties [41].

A new question arises when none of the monomers are anomalous, but one can be modeled with a TLS potential without competition between the scales. For instance, soft colloidal [42,43], metallic/polymer [44,45] and liquid–crystal/polymer [46] Janus dumbbells have a colloidal monomer whose interaction can be described by a TLS potential [47] and a monomer that have OLS interaction.

In order to answer this question, we explore the pressure versus temperature phase diagram of a model system. The system is composed by Janus particles where one monomer interacts through a TLS potential without anomalies and the other monomer interacts through an LJ potential. We investigate how the presence of the LJ monomer affects the competition between the two characteristic distances, the self-assembly structures and describe qualitatively the thermodynamic phases.

The paper is organized as follows. The model, the methods and simulation details are described in Section 2; the results and discussion are given in Section 3; and then the conclusions are presented in Section 4.

2. The model and the simulation details

In this paper, all the physical quantities are computed in the standard LJ units [48],

$$r^* \equiv \frac{r}{\sigma}, \quad \rho^* \equiv \rho\sigma^3, \quad \text{and} \quad t^* \equiv t \left(\frac{\epsilon}{m\sigma^2} \right)^{1/2}, \quad (1)$$

for distance, density of particles and time, respectively, and

$$p^* \equiv \frac{p\sigma^3}{\epsilon} \quad \text{and} \quad T^* \equiv \frac{k_B T}{\epsilon} \quad (2)$$

for the pressure and temperature, respectively, where σ is the distance parameter, ϵ the energy parameter and m the mass parameter. Since in the present work all physical quantities are expressed in reduced LJ units, we will omit the * for simplicity.

N dimers were used in each simulation, in a total of $2N$ particles. Each monomer has diameter σ and mass m , and the Janus dumbbells are constructed using two monomers linked rigidly at a distance $\lambda = \sigma$. The only difference between the monomers is their interaction. Monomers of type A interact with another A monomer through a TLS core-softened potential, proposed by da Silva and co-workers [17]

$$\frac{U^{\text{TLS}}(r_{ij})}{\epsilon} = 4 \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + u_0 \exp \left[-\frac{1}{c_0^2} \left(\frac{r_{ij} - r_0}{\sigma} \right)^2 \right] - u_1 \exp \left[-\frac{1}{c_1^2} \left(\frac{r_{ij} - r_1}{\sigma} \right)^2 \right], \quad (3)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between two A particles i and j . This equation has three terms: the first one is the standard LJ 12–6 potential [48], the second is a Gaussian centered at $r_0 = 0.70$, with depth $u_0 = 5.0$ and width $c_0 = 1.0$, responsible for the shoulder in the potential shape, and the last term is also a Gaussian, but centered at $r_1 = 3.0$, with depth $u_1 = 1.0$ and width $c_1 = 0.5$, responsible for the attractive well in the potential, as indicated in Fig. 1 by the solid red line. Despite the

Download English Version:

<https://daneshyari.com/en/article/974277>

Download Persian Version:

<https://daneshyari.com/article/974277>

[Daneshyari.com](https://daneshyari.com)