ARTICLE IN PRESS

Physica A ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at SciVerse ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Liquid crystalline and solid phases for a system of hard zigzag particles with Lennard-Jones sites in two-dimensions

Fidelmar Lechuga-Sanabria [a], Gustavo A. Chapela [b], Jacqueline Quintana-H [a,*]

[a] Instituto de Química, Universidad Nacional Autónoma de México, Apdo. Postal 70213, 04510 Coyoacán, México, D.F., Mexico

[b] Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco 186, Col. Vicentina, 09340 México, D.F., Mexico

HIGHLIGHTS

- Comparison of 2 chiral models, only repulsions and repulsions + attractions.
- The attractive sites are modeled via Lennard-Jones potentials.
- Nematics appear in both models, while smectics only in the hard model.

ARTICLE INFO

Article history:
Received 21 March 2013
Available online xxxx

Keywords:
Molecular simulations
Liquid crystals
Two-dimensional systems

ABSTRACT

The map of low and high density phases of an idealized system, the infinitely hard zigzag line model with two Lennard-Jones (LJ) sites is presented. LJ sites are added to a previous model composed of the infinitely hard zigzag line shape particles, R.A. Perusqía, J. Peón, J. Quintana, Physica A 345 (1) (2005) 130–142. The attractions and the molecular volume added to this system through the LJ sites create a more realistic model and, as a consequence, a richer phase behavior is obtained. Although the volume of the LJ sites is quite small it is enough to produce solid phases, absent in the original model. On the other hand the smectic phase that was present in the hard system was not found in this case. Two molecular conformations are chosen to provide a comparison with the previous model. The isothermal–isobaric is used to establish the thermodynamic regions of the different molecular self aggregations and to compare them to already published results.

1. Introduction

Recently, interesting results in the liquid crystal area have been found from chemical synthesis [1], in particular, searching for specific applications. Among the molecular shapes identified as liquid crystals, the calamitic shape is probably the most studied being the first recognized for producing mesophases. Other molecular geometries like the discotic shape [2] or the bent shape [3] have been also acquired special importance. For example, bent-core liquid crystals, exhibit spontaneous or induced (by electric fields) polarization, another important property of this kind of liquid crystals is their ability to generate supramolecular chirality. Despite the fact that the molecular symmetry of calamitics and discotics can be idealized as cylindrical, the results show that the difference in molecular anisotropy, measured as the molecular aspect ratio, in general gives rise to quite different optical and electrical properties. On the other hand, the bent shape was very recently acknowledged as a class of liquid crystals [4] by its difference in molecular symmetry with respect to the calamitics or discotics. An important fact is that all of these different molecular conformations seem to produce several kinds of phase structures with various macroscopic characteristics.

* Corresponding author. Tel.: +52 55 5622 4510; fax: +52 55 5616 2217.
E-mail addresses: jaq@unam.mx, jaq5tana@yahoo.com (J. Quintana-H).

0378-4371/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physa.2013.05.034

Molecular simulations have been very useful to advance in the understanding of how molecular geometry affects the phase structure. Different kinds of models have been studied and provided important knowledge about how the details in the interactions produce a specific mesophase [5,6]. One scheme that has been taken into account in the construction of the models is the partition of the molecular interactions as repulsions and attractions, originally proposed by van der Waals [7] and successfully applied to liquid crystals by Onsager [8]. One possible route to start studying the formation of liquid crystalline mesophases is to consider in the first place the anisotropy associated to the repulsive part of the intermolecular potential. In a second instance, attractions are included, either as short ranged forces like those in the van der Waals scheme or as long ranged interactions like the electrostatic scheme. In particular, short range interactions are of wide interest because of the important role they play in Physics, Chemistry and Biological disciplines [9]. Some examples about the importance of this kind of interactions can be found in condensed matter phases like molecular crystals [10], liquid state [11], liquid crystalline mesophases [12], molecule/substrate interactions [13], intermolecular complexes [14] and structural conformation of biomolecules [15]. Short ranged interactions are not only important in the description of the chemical nature of complex systems, but also they offer an opportunity to mimic them in order to develop technological applications and pharmaceutical drugs.

A quite common way to include the van der Waals forces is using the LJ potential which has been employed to describe a wide variety of systems [16]: For example, simulation of polymers [17], dendrimers [18], adsorption of several kind of molecules to surfaces and zeolites [19], crystallization processes [20], formation of liquid crystalline mesophases [21], chemical reactions [22], liquid–vapor equilibrium of organic molecules [23].

It is known that dimensionality affects the macroscopic properties of physical–chemical systems [24], particularly the structure of phase diagrams. Important theoretical results have provided some examples where the dimensionality produces the presence of a mesophase and therefore the phase diagram is modified [5,21]. However there is one case that has led to a change in the understanding of condensed matter. This is the Kosterlitz–Thouless (KT) phase transition where a peculiar mechanism takes place based on the association–dissociation of vortices [25] occurring over a whole range of finite temperatures. The KT type of mechanism has been applied to the melting process in two-dimensions for some systems [26]. The lack of long range translational order emerges as the remarkable conclusion. Previous results [27] have also pointed out the impossibility of having translational long range order in two dimensions for most cases. Straley [28] has also shown the impossibility of having long range order for separable intermolecular potentials, while for non-separable potentials it cannot be said a priori if there is quasi or long range order. From the experimental point of view, there have been a number of situations reported where this issue produces major changes in the phase diagram. The confinement of molecules to a plane, breaks part of the symmetry rules and allows self-interactions to take place [29], resulting in the formation of highly ordered planar structures. Self assembled monolayers of chainlike molecules on metallic films [30], surfactants adsorbed in air/water or oil/water interfaces [31], catalysis [32] and biological recognition of biomolecules like proteins and antigens over several substrates [33], are some examples of two dimensional (2D) interactions.

Structural characterization of surfaces is made principally using a Scanning Tunneling Microscope [34]. However the small size of the constituent molecules of layers, is the principal obstacle in the characterization process with this methodology due to insufficient resolution. Numerical simulations are a useful tool to study the formation of monolayers taking into account the molecular interactions and their influence in the construction of 2D molecular layers. As a consequence, there can be some detailed experimental routes plotted to build supramolecular structures, and ultimately to save experimental efforts [35].

In this paper the formation of 2D solids and liquid crystalline phases of linear zigzag systems with short range attractions modeled by the LJ potential is described. Different thermodynamic conditions are studied and a few simulation routes using Monte Carlo in the isothermal–isobaric, canonical and Gibbs ensemble are followed. Characterization of the different phases is done by calculating the equation of state $\rho = \rho(p)$, the nematic order parameter S and the radial distribution functions $g(r)$, with the goal of testing how small changes in the way of modeling the interactions between particles affect the structure of resulting phases. A comparison with the previous version of the model, the infinitely hard system [36], is discussed. The paper is organized as follows: the molecular model is defined in Section 2, simulation details are presented in Section 3, results can be found in Section 4 and the conclusions are in Section 5.

2. Definition of the molecular model

The model is defined by three line segments, the central segment that will be known as the body B and the two end segments or arms A, where the relation $L = 2A + B = 1$ holds. The angle between B and A is θ as shown in Fig. 1. At the junctions between A and B one LJ site is located. Interactions between LJ sites are considered only for intermolecular cases and are defined according to the following Eq. (1):

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \tag{1}$$

where $\sigma/L = 0.1$ and $\epsilon/k = 1$ The subscripts $i, j = 1, 2$ denote sites for unlike molecules.

The interaction between a pair of segments is infinitely repulsive and the interaction segment-LJ is taken as infinitely hard. Two values of A are studied, $A = 0.15, 0.25$ and the angle is $\theta = \pi/4$.

Please cite this article in press as: F. Lechuga-Sanabria, et al., Liquid crystalline and solid phases for a system of hard zigzag particles with Lennard-Jones sites in two-dimensions, Physica A (2013), http://dx.doi.org/10.1016/j.physa.2013.05.034