Journal of Molecular Liquids 185 (2013) 26–31

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

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

Structural properties of hockey stick-shaped particles in two dimensions

J.A. Martínez-González [a], S. Varga [b], P. Gurin [b], J. Quintana-H [a,]*

[a] Instituto de Química, Universidad Nacional Autónoma de México — Apdo. Postal 70213, 04510, Coyoacán, México D.F., Mexico
[b] Institute of Physics and Mechatronics, University of Pannonia, PO Box 158, Veszprém H-8201, Hungary

ARTICLE INFO

Keywords:
Liquid crystals
Monte Carlo simulations
Onsager theory
Bended nematics

ABSTRACT

Phase transitions and structural properties of the two-dimensional systems of hockey stick-shaped molecules have been examined by means of Monte Carlo simulations and the Onsager-theory. The hockey stick-shaped particles are modeled as hard bent-core needles. Isotropic–nematic and nematic–smectic antiferroelectric structural changes are observed. Spontaneously bended nematic structures are also found for such molecular shapes where the lengths of the segments are similar. The agreement between Monte Carlo and Onsager results is satisfactory.

1. Introduction

Despite the fact that the bent core particles have been synthesized since about 1930 by Vorländer [1], it was not until the last years when the importance of V-shape molecules was recognized in the liquid crystal area. One of the main findings about this molecular shape was reported by Niori et al. [2]. It was believed that the presence of chiral molecules in the smectic C phase was necessary to develop ferroelectricity. However it was shown that achiral molecules with bent core shape, called bananas, can produce polar phases [2]. Another interesting characteristic is that achiral molecules like bananas, can generate chiral phases [3]. After these two discoveries, many experimental studies have been dedicated to the synthesis of banana molecules. Bent core particles are good candidates for applications, for example, the fabrication of stable liquid crystal fibers [4]. Also the polar switching by the application of an electric field makes the banana molecules appropriate for constructing electronic displays [1,5].

Many experimental studies have been dedicated to the synthesis of banana-shaped molecules searching for different mesophase characteristics [4,6]. However, more recently a new kind of banana-shape particle has been produced, the hockey stick-shaped molecules [7], where the length of both segments is not the same. Lately, several syntheses have been proposed where the sizes of the segments are changed to generate different phase diagrams [8]. Chemical modifications are performed to produce materials with special phase transitions sequences at specific ranges of temperatures, which may lead to the design of materials with well defined characteristics. In particular, the generation of nematic (N), smectic A (Sm A) and smectic C synclinic (Sm Cs) and anticlinic (Sm Ca) and their transition temperatures. Because of the particular shape, these molecules may share characteristics of the calamitics and of the bent core molecules [9]. Their bent shape enhances the formation of layered structures (smectic) if the density of the system is high enough. On the other hand, depending on the ratio of the segment's lengths and the angle between the segments, these bodies can be more anisotopic than the bananas and, therefore able to produce the nematic phase. It is well accepted that molecular shape has an important effect on the phase diagrams and physical properties [9,10]. In this respect, molecular simulations can contribute to this kind of knowledge.

There is one important difference between hockey stick-shaped and banana-shaped molecules. Although, the hockey stick-shaped and the banana-shaped molecules are achiral, the confinement of these molecules into a flat surface makes the hockey stick-shaped bodies chiral, while the banana remains achiral.

Several simulation and theoretical studies have been devoted to understand the phase behavior of bent core particles [11–16].

However, we are not aware of any theoretical and simulation studies for two-dimensional hockey stick-shaped particles. Chemical synthesis is in general a hard task, therefore it is important to propose and to study different molecular conformations in order to suggest particular molecular shapes that may give rise to interesting properties. Recently in the nanotechnology area, hockey stick-shaped conformations for nano scale objects have been investigated to build nanomachines [17].

The paper is organized as follows. Section I contains the introduction, the model and the details of simulations are contained in section II. Results are presented in Section III and finally section IV is dedicated to conclusions.

2. Monte Carlo simulations

A two-dimensional hard body model whose shape mimics the Hokey stick (HS) molecules is studied. Our model particle consists of two line segments of unequal length. The length of the segments

---

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

0167-7322/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2012.11.020

is a and b, i.e. the total length of the model particle is $L=a+b$. The model is sketched in Fig. 1.

Our previous hard banana study ($a=b=1/2$) [11] has been extended by examining the chiral hockey stick-shaped needles at $a=$ 0.4, 0.333, 0.25, 0.175 and 0.125. Note that the total length of the particle is $L=1$, i.e. $b=1-a$. The total number of particles in the simulation cell is $N=1000$.

The simulations have been performed in the isobaric and isochoric ensembles. Periodic boundary conditions were applied to both axis of the simulation box and the minimum-image criterion was also considered. The density was defined as $\rho^*=N/(L_x^* * L_y^*)$ where L_x^* and L_y^* are the simulation box length for x and y axes respectively and L is used to make the lengths dimensionless. The dimensionless pressure is defined as $p^*=p\beta L^2$ where $\beta=1/k_BT$ and k_BT is the Boltzmann constant. Because the model is athermal the temperature has been set to $k_BT=1$.

The movements performed in the isochoric ensemble consist of random changes in the position or orientation of the particles. In the isobaric simulations, besides the displacements or rotations, changes in the area of the simulation box are allowed too [18]. In general one change of area is done every $5N$ displacements or rotations. In this work, this is called a cycle. The standard Metropolis criterion was used to accept or reject the new configurations, in addition the maximum values allowed for each kind of movement were modified during the simulations to get a 30% acceptance rate. The isobaric simulations were used to obtain the equation of state and the polar and non-polar nematic order parameters, while isochoric simulations were used to generate the positional distribution function, $g(r)$, and the orientational correlation function, $g_2(r)$.

For all isobaric simulations, a compression process starting with a pressure small enough to have an isotropic equilibrated configuration was used. The pressure was increased slowly and for each pressure the initial configuration was the final one of the previous pressure. Approximately 10^6 Monte Carlo cycles were required to assume equilibrium and other 10^5 to obtain averages.

The nematic order parameter, S, is given by the largest eigenvalue of the traceless symmetric tensor $T_{ij}=2\langle\omega_i\omega_j\rangle-\delta_{ij}$. "$\langle\rangle$" denotes an ensemble average, δ_{ij} is the Kronecker delta function and ω_i is the i-component of the orientational unit vector. It is well known that for finite size systems, S depends on the number of particles, and for hard straight needles it goes to zero in the thermodynamic limit. Instead of long range order, quasi long range order takes place, as a result the orientational correlation function defined as $g_2(r)=\langle\cos(2\phi(0)-2\phi(r))\rangle$ changes its behavior from an exponential decay (isotropic phase) to an algebraic decay (nematic phase) [19]. The change from exponential to algebraic decay serves as the critical density of the isotropic–nematic continuous transition.

Although the change from exponential to algebraic decay in the correlation functions is an indication of the Kosterlitz–Thouless (KT) phase transition [20], which is typical in 2D systems, this cannot be taken strictly as a sufficient condition to assure a KT type. A more detailed study of the change of some properties would be required when the system size increases. For example, such as to verify the non singular behavior of the heat capacity and that the nematic order parameter $S\to 0$ when $N\to\infty$.

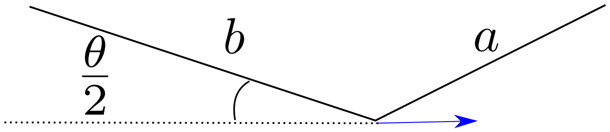

Fig. 1. Hard body representation of a hockey stick-shaped (HS) molecule consisting of two line segments with $a+b=L=1$ and a bend angle θ between them. The arrow does not belong to the particle, it represents its polar axis.

3. Onsager's theory

In the frame of the Onsager theory the Helmholtz free energy is written as the sum of an ideal energy and an excess contribution:

$$\frac{\beta F}{A}=\frac{\beta F_{\mathrm{id}}}{A}+\frac{\beta F_{\mathrm{ex}}}{A}, \tag{1}$$

where A is the total area.

The ideal part of the nematic free energy is given by

$$\frac{\beta F_{\mathrm{id}}}{A}=\rho\ln(\rho)-\rho+\rho\sigma[f], \tag{2}$$

where $\sigma[f]=\int_0^{2\pi}\mathrm{d}\phi f(\phi)\ln(2\pi f(\phi))$, ρ is the number density, ϕ is the angle between the molecular axis and the y-axis and $f(\phi)$ is the orientational distribution function (ODF). For a hard potential the excess free energy is,

$$\frac{\beta F_{\mathrm{ex}}}{A}=\frac{1}{2}\rho^2\int_0^{2\pi}\mathrm{d}\phi_i f(\phi_i)\int_0^{2\pi}\mathrm{d}\phi_j f\left(\phi_j\right)A_{\mathrm{exc}}(\gamma), \tag{3}$$

where $A_{\mathrm{exc}}(\gamma)$ is the excluded area and $\gamma=\phi_i-\phi_j$. As a consequence, the free energy becomes

$$\frac{\beta F}{A}=\rho\ln(\rho)-\rho+\rho\sigma[f]+\frac{1}{2}\rho^2\int_0^{2\pi}\mathrm{d}\phi_i f(\phi_i)\int_0^{2\pi}\mathrm{d}\phi_j f\left(\phi_j\right)A_{\mathrm{exc}}(\gamma). \tag{4}$$

If the ODF and the excluded area are written as their Fourier series $f=\sum_i f_i cos(i\phi)$ and $A_{\mathrm{exc}}=\sum_i a_i cos(i\phi)$, where f_i and a_i are the Fourier coefficients of the ODF and the excluded area, then the free energy becomes

$$\frac{\beta F}{A}=\rho\ln(\rho)-\rho+\rho\ \sigma[f]+\frac{1}{2}\rho^2\left\{a_0+\sum_{j=1}^{N}f_j^2\,a_j\pi^2\right\}. \tag{5}$$

The ODF-coefficients are those that minimize the free energy. In the isotropic phase $f_0=1/2\pi$ and the higher order terms are zero. In the nonpolar nematic phase the even terms (f_2, f_4,...) are nonzero, while for the polar nematic phase both the even and the odd terms are nonzero.

For a weak nematic order the first nonvanishing term can be either f_1 or f_2. In the polar nematic phase f_1 is nonzero, and it can be derived from Eq. (5) that the polar free energy is $\frac{\beta F_p}{A}\cong\frac{\beta F_{\mathrm{iso}}}{A}+\rho\pi^2 f_1^2+\frac{1}{2}\rho^2 f_1^2 a_1\pi^2$, where $\beta F_{\mathrm{iso}}/A$ is the free energy of the isotropic phase. For nonpolar phase f_2 is the first nonvanishing term and we can get from Eq. (5) that $\frac{\beta F_a}{A}\cong\frac{\beta F_{\mathrm{iso}}}{A}+\rho\pi^2 f_2^2+\frac{1}{2}\rho^2 f_2^2 a_2\pi^2$. Note that the second term of the above equations comes from $\sigma[f]$.

At the isotropic–nematic bifurcation the isotropic and the nematic free energy must be equal, therefore we end up with the following equations for the bifurcation density

$$\rho_{\mathrm{bif}}^{\mathrm{IN}}=\min\left\{-\frac{2}{a_1},-\frac{2}{a_2}\right\}. \tag{6}$$

We have not observed polar bifurcation in our calculations, i.e. the isotropic phase transforms into nonpolar nematic phase with increasing density for all studied molecular shapes.

For the nematic–smectic antiferroelectric phase transition, a version of the theory was developed in the limit of perfect nematic order, when all particles are parallel. To take the effect of the orientational entropy into account, we consider the binary mixture of the particles, where the particles' orientations of the components are opposite. For such system, each orientation corresponds to a specific geometric polarity; in this light, we have a mixture of particles