Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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M. Ishitobi [a]

[a] Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., 6 Kitahara, Tsukuba, 300-3294, JAPAN

Version of record first published: 27 Oct 2006

To cite this article: M. Ishitobi (2001): A Novel Monte Carlo Method for Liquid Crystal using Extended Inter-Molecular Potential (EIMP), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 785-788

To link to this article: http://dx.doi.org/10.1080/10587250108025357

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 785-788
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A Novel Monte Carlo Method for Liquid Crystal using Extended Inter-Molecular Potential (EIMP)

M. ISHITOBI

Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd. 6 Kitahara, Tsukuba, 300–3294, JAPAN

A novel Monte Carlo (MC) simulation method using Extended Inter-molecular Potential (EIMP) for liquid crystal (LC) systems is reported. The EIMP is calculated, prior to the MC calculation, as interaction energy between two molecules that are located in various configurations. The MC method using the EIMP enables to carry out a calculation of even a system within many molecules in short CPU time. It is applied to the systems that consist of 750 – 1000 molecules of typical LCs (4-n-alkyl-4′-cyanobiphenyls; nCB's). Several phases are successfully reproduced and order parameters of them agree with the experiments.

Keywords: Monte Carlo simulation; extended inter-molecular potential; order parameter

1. INTRODUCTION

Increasing computer power, the molecular simulation becomes an important tool to examine the dynamic and static microscopic properties of materials. In liquid crystal (LC) study, various models of a molecule for the simulation are proposed. They are roughly classified into two groups of the simplified rod and the atom-based models.

The simplified rod model, such as a cylinder, a disk, the Gay-Berne molecule etc., extracts the anisotropy of a molecule in shape that is one of the essences of LC. Because of its simplicity, a calculation of a large system can be carried out in short CPU time

easily.

On the other hand, the atom-based model can represent flexible motions from molecular structure. It also can include differences of chemical substitutes of molecules, which are important in the molecular design. But it requires longer CPU time than the former on account of a lot of interacting points that are usually atoms or groups of atoms; the interacting point in the former model is only one in a molecule.

Recently new model as a combination of above two types is appeared [1]-[3]. It has rigid Gay-Berne cores and flexible alkyl chains that consist of CH_2 Lennard-Jones spheres. It realizes a calculation of a system within a lot of molecules and in short CPU time at the same time.

Our model, the extended inter-molecular potential (EIMP), is also developed from the viewpoint of a coarse grained picture of a molecule. We will show in the following section that the EIMP treats a molecule as a rod with complex surface that reflects a complex molecular conformation. For a system of real molecules, a simulation using the EIMP gets a light calculation as same as a conventional simplified rod model.

2. METHOD

In the EIMP method a molecule is expressed a rigid body with some conformation that is an average shape at a specific temperature. We produce the average conformation though molecular dynamic calculations for a system of several molecules using usual atom-based potentials.

The EIMP is estimated from interaction energy E between two molecules (they are called A and B here) that have the above average conformation as following.

$$E = \Sigma_{ij} (a_{ij} / r_{ij}^{9} - b_{ij} / r_{ij}^{6} + e_{ij} / r_{ij}).$$

Here, r_{ij} is a distance between the atom i (in the molecule A) and the atom j (in the molecule B), a_{ij} and b_{ij} are parameters of the van der Waals potential, e_{ij} is a parameter of the electro-static potential. We use pcff potential parameters [5].

The interaction energy E is a function of the configuration of the two molecules. The molecule A is set on the origin of the coordinates and parallel to the z-axis. The

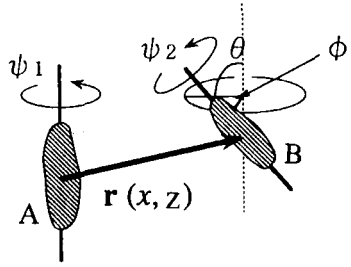

FIGURE 1. Determination of configuration

molecule B is on the various points and directions. The relative configuration of the A and B is written by six variables (see Fig. 1) ; x and z are the components of the displacement between A and B's center of the gravity, θ and ϕ are the angles of the precession of B, ϕ_1 and ϕ_2 are the angles of the rotation around the molecular axis, respectively.

It is assumed that the rotational motion around the molecular axis is free and enough faster than the orientational relaxation in isotropic, nematic and some smectic phases. This assumption says that a molecule feels an average potential on the rotation from surrounding molecules in the time scale of the orientational relaxation. According to this thought, the EIMP is determined the average E over ϕ_1 and ϕ_2 as following.

$$E_{\mathrm{EIMP}} = < E(x, z, \theta, \phi) >_{\phi 1, \phi 2}$$

For various configuration (x, z, θ , ϕ), we calculate E_{EIMP} and save it into a electric file in a computer (we call this file the EIMP map). We can estimate inter-molecular potential between two molecules that locate any configuration using the EIMP map through the interpolation.

In a Monte Carlo (MC) calculation for a system within many molecules, the potential energy of the system is a sum of inter-molecular potential between all of the pairs of the molecules, which is extracted from the EIMP map.

Isothermal-isochoric MC calculations are carried out for systems of 750 molecules under the periodic boundary condition. The initial state has a large enough cell and random locations of the molecules (nearly gas phase). The cell is kept in a cubic shape and is compressed step by step.

3. RESULTS

We apply the EIMP-MC method to systems within 750 molecules of cyanobiphenyl (0CB) and methyl - cyanobiphenyl (1CB) at 400K. At 400K both materials of 0CB and 1CB show isotropic liquid experimentally [6] , [7] .

We would show the orientational order parameters S with previous results [4] in Fig. 2 (in previous calculation, 5CB and 8CB systems including 1000 molecules are used). These calculated S's show good agreement

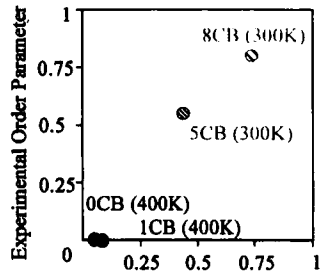

FIGURE 2. Comparison with calculated and experimental S

with experiments. As a result, in the series of nCB's the calculated S's display an almost linear correlation with experiments. In the case of 0CB system calculations the CPU time was required about two days on an XP1000 Unix machine (667MHz ; Compaq).

4. CONCLUSIONS

We apply the EIMP-MC method to some system of nCB series molecules. The orientational order parameters S show good agreement with experiments. This means that our assumption of the free rotation around the molecular axis in some liquid phases with low symmetry is good for nCB systems at least on orientational order.

5. ACKNOWLEDGMENTS

A part of this work was performed under management of Association of Super-Advanced Electronic Technologies (ASET) in the Ministry of International Trade and Industry (MITI) Program of Super-Advanced Electronic Technologies supported by New Energy and Industrial Technology Development Organization (NEDO).

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