

Three-dimensional rotational Langevin dynamics and the Lebwohl-Lasher model

Christophe Goze Bac

Groupe de Dynamique des Phases Condensées, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

Ricardo Paredes V. , Carlos Vásquez R., Ernesto Medina D., and Anwar Hasmy

Laboratorio de Física Estadística de Sistemas Desordenados, Centro de Física, IVIC, Apartado 21827, Caracas 1020A, Venezuela

(Received 14 November 2000; published 21 March 2001)

We introduce a new scheme for molecular-dynamics simulation of three-dimensional systems exhibiting rotational motions. The procedure is based on the Langevin dynamics method. Our paper is focused on the Lebwohl-Lasher model in order to simulate the isotropic-nematic transition of liquid crystals. In contrast to previous dynamic approximations, our approach allows one to reproduce well the isotropic phase of these systems.

DOI: 10.1103/PhysRevE.63.042701

PACS number(s): 64.70.Md, 83.10.Mj

The three-dimensional rotational motion of molecules arises in a variety of problems. Typical examples can be found in colloidal suspensions [1], ferroelectric fluids [2], and nematic liquid crystals [3,4]. Usually these systems involve dipolar interactions between molecules as in the case, for example, of the XYZ [5] and the Maier-Saupe [6] model. For nematic liquid crystals many computational works have considered a lattice version of the Maier-Saupe model called the Lebwohl-Lasher model [7], which is described by the following interaction:

$$U_i = - \sum_{j=1}^m \bar{J}_{ij} P_2(\mathbf{n}_i \cdot \mathbf{n}_j) = - \sum_{j=1}^m J_{ij} (\mathbf{n}_i \cdot \mathbf{n}_j)^2 + c, \quad (1)$$

where m is the number of nearest neighbors of the particle i , $\bar{J}_{ij} (= 3J_{ij}/2)$ is a positive coupling constant, P_2 is the second Legendre polynomial, c is a constant, and $\mathbf{n}_i = \sin \theta_i \cos \phi_i \mathbf{i} + \sin \theta_i \sin \phi_i \mathbf{j} + \cos \theta_i \mathbf{k}$ denotes the orientation vector at the site i . Usually, Monte Carlo (MC) techniques are used to bring the system to the equilibrium [7–11]. However, when one is interested in the relaxation mechanism or the dynamical behavior of the system a molecular-dynamics (MD) technique is required [12–15]. For these kinds of simulations, one method is based on the Langevin theory, namely, the Langevin molecular-dynamics simulations also called Brownian dynamics [16]. Such a MD method should be able to reproduce the isotropic-nematic phase transition and the typical isotropic phase of the liquid-crystal molecules observed at high temperature. This phase corresponds to a homogeneously random in orientation of all the molecules forming the sample. Within this technique, previous approaches have failed to describe this phase [14]. To our knowledge, a MD method able to recover this phase has never been worked out in detail.

In this paper we propose a new method to simulate systems described by a dipolar-dipolar interaction by means of Langevin dynamics (LD). We show that assigning a proper weight to each angular configuration is nontrivial in reproducing the right behavior and has been the source of recent confusion [14].

The Langevin equation is used to replace Newton equations when the problem is to simulate the motion of a system in contact with a thermal bath. In the noninertial limit, the one-particle Langevin equation for a system containing N interacting particles can be written as

$$\zeta \dot{x} = - \frac{\partial U}{\partial x} + R(x, t), \quad (2)$$

where \dot{x} , ζ , and $R(t)$ are the drift velocity of the particle moving in the bath, the drag coefficient of the particle, and the random (thermal) force, respectively. The function $R(x, t)$ is an uncorrelated random function (white noise) that obeys:

$$\langle R(x, t) R(x, t') \rangle = 2k_B T \zeta \delta(t - t'), \quad (3)$$

where k_B and T are the Boltzmann constant and the temperature. In practice, for discrete simulations we have

$$R(x, t) = \sigma \lambda_i(t), \quad (4a)$$

with

$$\sigma = \sqrt{2k_B T \zeta / \delta t}, \quad (4b)$$

where δt is the time interval and $\lambda_i(t)$ is a random number, picked from an uncorrelated random number generator with a Gaussian distribution centered at zero.

In spherical coordinates the three-dimensional rotational motion of molecules is described by the angles θ (with $0 \leq \theta \leq \pi$) and ϕ (with $0 \leq \phi \leq 2\pi$). Traditionally, when using the Metropolis Monte Carlo algorithm, a new configuration is proposed by generating the angles (θ, ϕ) for each molecule using a random number generator with a uniform distribution in $\cos \theta$ for a given temperature. This procedure considers the appropriate weights in the generation of the orientational configurations. In the case of the Langevin dynamical method, the strategy is not straightforward since the equations of motion contain a deterministic and a random term. Recently, this procedure was used by direct substitution of x in Eq. (2) with θ and ϕ [14]. As we will see below this approach fails to reproduce the phase transition and the

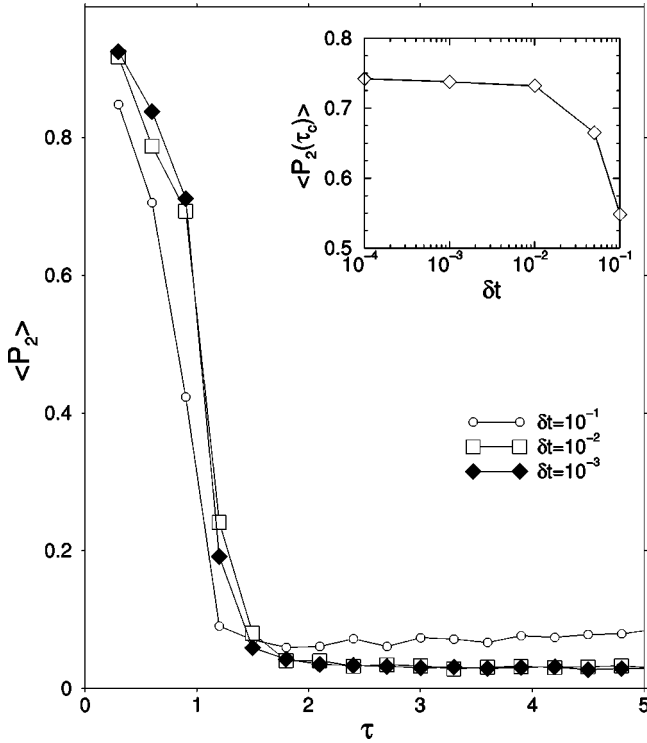


FIG. 1. Order parameter $\langle P_2 \rangle$ as a function of the reduced temperature τ for different integration step sizes δt (in units of \bar{J}/ζ). The inset shows the dependence of $\langle P_2 \rangle$ at the reduced critical temperature τ_c as a function of δt .

expected isotropic phase (the zero polarization phase). We considered the following equations of motion:

$$\zeta \frac{\partial \cos \theta}{\partial t} = - \frac{\partial U}{\partial \cos \theta} + R(\theta, t), \quad (5a)$$

and

$$\zeta \frac{\partial \phi}{\partial t} = - \frac{\partial U}{\partial \phi} + R(\phi, t). \quad (5b)$$

Differentiating $\cos \theta$ with respect to θ , and discretizing the above equations for a given molecule i one obtains

$$\begin{aligned} \theta_i(t + \delta t) = & \theta_i - \frac{\delta t}{\sin^2 \theta_i} \frac{\partial}{\partial \theta_{ij=1}} \sum_{j=1}^m J_{ij} [\sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j) \\ & + \cos \theta_i \cos \theta_j]^2 + \frac{\sqrt{2\tau\delta t}\lambda(\theta_i, t)}{\sin \theta_i}, \end{aligned} \quad (6a)$$

and

$$\begin{aligned} \phi_i(t + \delta t) = & \phi_i - \delta t \frac{\partial}{\partial \phi_{ij=1}} \sum_{j=1}^m J_{ij} [\sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j) \\ & + \cos \theta_i \cos \theta_j]^2 + \sqrt{2\tau\delta t}\lambda(\phi_i, t), \end{aligned} \quad (6b)$$

where θ_i and ϕ_i are the angles at time t , $\tau = k_B T / \bar{J}$ is the reduced temperature, and the time interval δt is considered

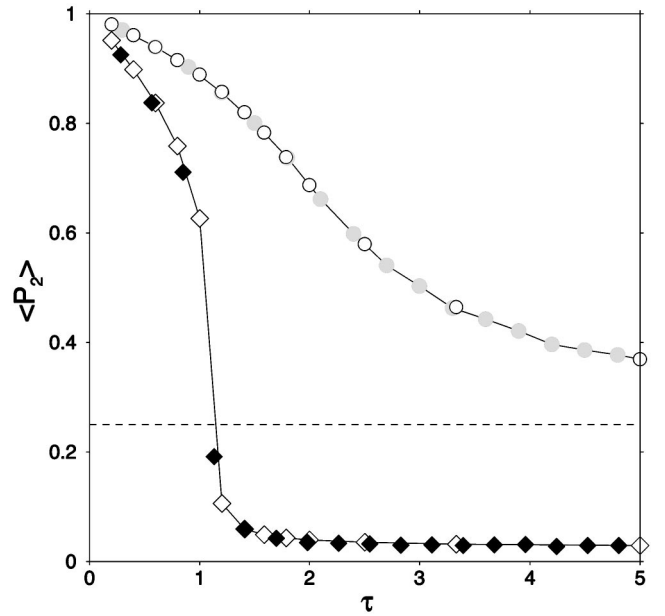


FIG. 2. Order parameter $\langle P_2 \rangle$: open and black diamonds correspond to results from MC and LD calculations, respectively, with uniform distributions of $\cos \theta$ and ϕ . Open and gray circles correspond to results from MC and LD, respectively, with an uniform distribution of angles θ and ϕ . For this case, the high-temperature limit 0.25 is shown as a dashed line.

in units of \bar{J}/ζ . Note that when $\sin \theta_i$ tends to 0 the Eq. (6a) becomes singular. In order to circumvent this singularity produced by a privileged system of reference, we rewrite the equations in a referential R' where the unit vector \mathbf{i}' is along \mathbf{n}_i , while \mathbf{j}' and \mathbf{k}' are obtained by a simple rotation of the referential R defined by the following unitary matrix T_i ,

$$T_i = \begin{pmatrix} \sin \theta_i \cos \phi_i & \sin \theta_i \sin \phi_i & \cos \theta_i \\ -\sin \phi_i & \cos \phi_i & 0 \\ -\cos \theta_i \cos \phi_i & -\cos \theta_i \sin \phi_i & \sin \theta_i \end{pmatrix}. \quad (7)$$

Each of the orientation vectors \mathbf{n}_j in the neighboring of a site i can be determined using $\mathbf{n}'_j = T_i \mathbf{n}_j$. This procedure allows us to calculate the angles θ'_j and ϕ'_j . In the referential R' , the equations of motion reduce to

$$\theta'_i(t + \delta t) = \delta t \left[\frac{\pi}{2} - \sum_{j=1}^m J_{ij} \sin 2\theta'_j \cos \phi'_j + R(\theta'_i, t) \right] \quad (8a)$$

and

$$\phi'_i(t + \delta t) = \delta t \left[\sum_{j=1}^m J_{ij} \sin 2\phi'_j \sin^2 \theta'_j + R(\phi'_i, t) \right], \quad (8b)$$

where the spurious singularity is eliminated. Once the orientation at $t + \delta t$ is calculated in R' , we simply use $\mathbf{n}_i = T_i^{-1} \mathbf{n}'_i$, ($T_i^{-1} = T'_i$) to calculate the time evolution in the referential R .

By taking into account the above procedure, we performed our simulations by considering a cubic lattice of size $L \times L \times L$ sites. Each site contains a molecule that interacts with its six nearest neighbors. Periodic boundary conditions are considered at the edge of the box. At the beginning, the molecules are randomly oriented. A quantity of interest is the average order parameter $\langle P_2 \rangle$, which gives an idea of the polarization of the system, and it is determined as

$$\langle P_2 \rangle = L^{-d} \left\langle \frac{1}{2} \sum_i (3 \cos^2 \Omega_i - 1) \right\rangle, \quad (9)$$

where Ω_i is the angle between the axis of the i th rotor molecule and the nematic director. Because of the nonbroken continuous symmetry of the orientational ordering, the direction of the nematic director varies and has to be determined during the simulation in order to calculate $\langle P_2 \rangle$. This is possible by a diagonalization of the tensor order parameter \mathbf{Q} [3]. Then, the instantaneous value of the order parameter is given by the largest eigenvalue of \mathbf{Q} . In nematic liquid crystals, we should expect that $\langle P_2 \rangle$ tends to one at low temperature consistent with the ordered phase observed in these systems. At high temperature $\langle P_2 \rangle$ should tend to 0, which is typical of the isotropic (disordered) phase, i.e., the molecules are homogeneously random in orientation. We computed $\langle P_2 \rangle$ as a function of the reduced temperature τ . The averages of P_2 were performed for time larger than $25\bar{J}/\zeta$ in order to insure that the calculation is done when the system reaches its equilibrium. Calculations were done until $t = 30\bar{J}/\zeta$ and for size $L = 10$.

Figure 1 shows the order parameter $\langle P_2 \rangle$ as a function of the reduced temperature τ for different integration step sizes δt . As expected $\langle P_2 \rangle$ tends to 1 and 0 at low and high temperatures, respectively. The inset illustrates how $\langle P_2 \rangle$ be-

haves at the critical reduced temperature value τ_c ($= 1.1232$ [8]) as a function of δt . Note that $\delta t = 10^{-3}\bar{J}/\zeta$ is small enough to provide reliable results. As expected $\langle P_2 \rangle$ tends to 1 and 0 at low and high temperatures, respectively.

We also performed Monte Carlo calculations for systems of size $L = 10$ in order to compare with the results obtained from the Langevin dynamics simulations. Figure 2 compares both $\langle P_2 \rangle$ curves, which are depicted by open (MC) and black (LD) diamonds. Note that both curves are quite similar suggesting that our Langevin dynamics approach recovers well the nematic and the isotropic phase of the liquid crystals.

Furthermore, we performed MC and LD simulations when the sampling of states is uniform in (θ, ϕ) as in Ref. [14], instead of $\cos \theta$. Figure 2 presents the results. The curves depicted by gray circles (LD) and the open circles (MC) are very similar. It is clear that the high-temperature tendency of $\langle P_2 \rangle$ approaches to $\frac{1}{2} (\frac{3}{\pi} \int_0^\pi \cos^2 x dx - 1) = 0.25$ instead of 0. In addition, the phase transition is smoother than with our approach. Thus, our results clearly demonstrate that for reliable results the variable to be considered is $\cos \theta$ instead of θ in the Langevin dynamics equations. This implies that in Langevin dynamics method, as in the Monte Carlo simulation, the right weight when selecting one of the possible configurations for a given temperature, should not be neglected. This is a general result relevant to Langevin dynamics (and other methods involving a random choice of states) in systems where rotational motions exist.

The numerical calculations were done on the computers of the CINES (France) and CeCalcula (Venezuela). Discussions with P. Colmenares and J.A. Gonzalez are gratefully acknowledged as is the support from the PCP Venezuelan-French exchange program.

-
- [1] J.R. Melrose, Phys. Rev. A **44**, R4789 (1991).
 [2] G. Ayton, M.J.P. Gingras, and G.N. Patey, Phys. Rev. E **56**, 562 (1997).
 [3] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
 [4] S. Singh, Phys. Rep. **324**, 107 (2000).
 [5] J.-M. Liu and G. Müller, Phys. Rev. A **42**, 5854 (1990).
 [6] W. Maier and A. Saupe, Z. Naturforsch. A **14A**, 882 (1959); **15A**, 287 (1960).
 [7] P.A. Lebowitz and G. Lasher, Phys. Rev. A **6**, 426 (1972).
 [8] Z. Zhang, O.G. Mouritsen, and M.J. Zuckermann, Phys. Rev. Lett. **69**, 2803 (1992).
 [9] T. Bellini, C. Chiccoli, P. Pasini, and C. Zannoni, Phys. Rev. E **54**, 2647 (1996).
 [10] J. Chakrabarti, Phys. Rev. Lett. **81**, 385 (1998).
 [11] J. Ilynyskiy, S. Sokolowski, and O. Pizio, Phys. Rev. E **59**, 4161 (1999).
 [12] A. Pękaliski, J. Phys. A **24**, 1253 (1991).
 [13] A. Darinsky, A. Lyulin, and I. Neelov, Makromol. Chem. **2**, 523 (1993).
 [14] Z. Bradač, S. Kralj, and S. Žumer, Phys. Rev. E **58**, 7447 (1998).
 [15] J.L. Billeter, A.M. Smondyrev, G.B. Loriot, and R.A. Pelcovits, Phys. Rev. E **60**, 6831 (1999).
 [16] D.W. Heermann, *Computer Simulation Methods* (Springer-Verlag, Berlin, 1990).