Computer simulation of anisotropic molecular fluids*

J. Kushick[†] and Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

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We have extended the molecular dynamics method to permit the simulation of systems containing cylindrically symmetric molecules with arbitrary eccentricity. This extension is accomplished by means of a potential energy function which models the primary interaction effects of molecular anisotropy, and which is mathematically convenient for computer use. The method is then applied to two problems, one involving the stability of the nematic liquid crystal phase, and the other illustrating the effect of cooperative reorientation on spectral line shapes.

INTRODUCTION

The technique of computer simulated molecular dynamics has proven to be a useful aid to our understanding of the relationships between the motion of individual molecules and the observable properties of matter. Given a postulated intermolecular potential energy function, one numerically integrates the classical equations of motion for an assembly of 10^2–10^3 molecules and thereby obtains a trajectory in phase space containing detailed microscopic information about the molecular system. Statistical mechanics then enables one to use the phase space trajectory to calculate a variety of quantities of physical interest.[1]

The complexity of intermolecular potential functions for polyatomic molecules has limited the application of molecular dynamics to systems consisting of relatively simple molecules. Most molecular dynamics simulations performed thus far have dealt with spherically symmetric particles. Some work has also been carried out on molecules such as N_2, CO, and H_2O.[2-4] In these studies, molecular anisotropy was modeled through the use of expressions for dipolar and quadrupolar interactions and through the use of force centers located on individual atomic sites on the molecule. In the latter case, the total interaction of two molecules is a sum of atom–atom interaction terms. We know of no molecular dynamics study to date, however, of molecules with substantial anisotropy.

In this article, we describe a method for modeling the interactions of cylindrically symmetric molecules of arbitrary anisotropy. The model is based on an intuitive picture of the primary effects of molecular anisotropy on the interaction potential. Our method is sufficiently simple that it may easily be incorporated in a molecular dynamics program, and yet it is sufficiently flexible to allow the simulation of highly elongated particles. As a result, one may probe the dynamics of reorientation and the effects of anisotropic molecular structure under a variety of conditions.

The details of the modeling procedure are briefly described in the following section. In the remainder of the paper, we shall discuss two applications of the method. The first of these involves a search for the conditions of molecular eccentricity and density necessary for the existence of a stable nematic liquid crystal phase. The second application is an analysis of cooperative effects in reorientation. Such effects are important in the interpretation of depolarized Rayleigh light scattering in liquids. In addition, two applications of our method have been reported previously.[5,6] These involved the dynamics of angular velocity relaxation and the relative importance of the repulsive and attractive parts of the Lennard-Jones potential in self-diffusion.

THE MODEL

Berne and Pechukas have recently proposed a Gaussian overlap model of the interaction of two cylindrically symmetric molecules.[7] Each molecule is envisioned as an ellipsoid of revolution whose spatial orientation is specified by a unit vector $\hat{u}$ parallel to the molecule's major axis. Each molecule is characterized by a three dimensional Gaussian distribution of force centers, characterized by a length $\sigma_\parallel$ parallel to $\hat{u}$ and a width $\sigma_\perp$ perpendicular to $\hat{u}$. The interaction energy of two molecules is modeled by evaluating the overlap integral of their two associated Gaussians (see Fig. 1). When evaluated the integral I is seen to depend on a strength parameter ϵ and a range parameter σ which are analytical functions of the relative position and orientation of the two molecules.

$$I = \epsilon(\hat{u}_1, \hat{u}_2) \exp[-r^2/\sigma^2(\hat{u}_1, \hat{u}_2, \hat{r})] ,$$

$$\epsilon(\hat{u}_1, \hat{u}_2) = \epsilon_0 [1 - \chi^2 (\hat{u}_1 \cdot \hat{u}_2)^2]^{-1/2} ,$$

$$\sigma(\hat{u}_1, \hat{u}_2, \hat{r}) = \sigma_0 \left\{ 1 - \tfrac{1}{2}\chi \left[\frac{(\hat{r}\cdot\hat{u}_1 + \hat{r}\cdot\hat{u}_2)^2}{1+\chi(u_1\cdot u_2)} + \frac{(\hat{r}\cdot\hat{u}_1 - \hat{r}\cdot\hat{u}_2)^2}{1-\chi(\hat{u}_1\cdot\hat{u}_2)} \right] \right\}^{-1/2} .$$

Here, χ is determined by the anisotropy of the ellipsoids; if $a = \sigma_\parallel/\sigma_\perp$, then

$$\chi = (a^2 - 1)/(a^2 + 1) .$$

$\hat{u}_1$ and $\hat{u}_2$ are the orientation vectors of the two molecules. **r** is a vector joining the two centers; it has magnitude r, and $\hat{r} = \mathbf{r}/r$. ϵ_0 and σ_0 are scaling parameters.

The parameters ϵ and σ reflect the spheroidal symmetry of the molecules. It is then possible to use these orientation dependent parameters in any of the variety of two-parameter potentials which has been proposed to describe atomic interactions.

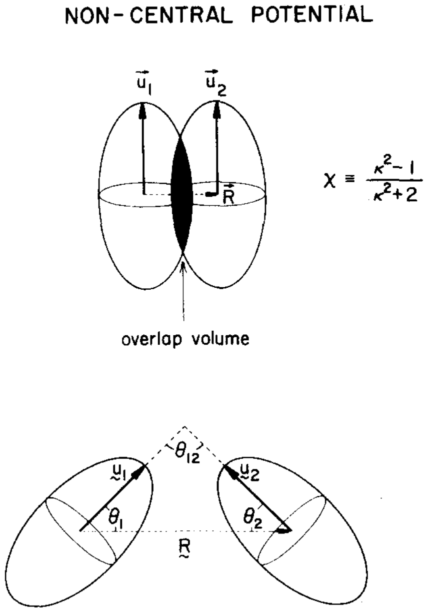

FIG. 1. The geometrical significance of the parameters used in defining the overlap potential. $\kappa \equiv a$ is the axial ratio.

We have used the σ and ϵ generated by the Gaussian overlap model in the Lennard-Jones 12-6 potential:

$$V(\hat{u}_1, \hat{u}_2, \mathbf{r}) = 4\epsilon(\hat{u}_1, \hat{u}_2)\left\{\left(\frac{\sigma(\hat{u}_1, \hat{u}_2, \hat{r})}{r}\right)^{12} - \left(\frac{\sigma(\hat{u}_1, \hat{u}_2, \hat{r})}{r}\right)^{6}\right\} .$$

By this means we construct a differentiable potential energy function which depends realistically on the distance between the molecular centers, and whose dependence on molecular orientation is based on a geometrically intuitive model. Molecules of any eccentricity may be handled with equal ease, since the expressions for σ and ϵ incorporate the length to width ratio of the molecule. This feature distinguishes our potential from multiple force center potentials such as that due to Corner, which become unwieldy at large eccentricity.[8] Furthermore, the fact that the orientation dependent Lennard-Jones potential is differentiable makes it very convenient for molecular dynamics calculations, as opposed to a hard ellipsoid model or the Kihara potential.[9] We therefore consider the model a useful tool in the examination of the properties of anisotropic systems.

STUDIES OF THE STABILITY OF NEMATIC ORDERING

Nematic liquid crystals are characterized by the long range rotational order of their constituent molecules, while they retain the translational disorder found in ordinary liquids. This ordering results in experimentally observed anisotropy in the mechanical and optical properties of nematic substances.[10]

The nematic state is observed in dense systems of elongated molecules. One may therefore surmise that nematic ordering is primarily a consequence of steric hindrance to molecular reorientation.[11] There has been some recent experimental evidence in support of this interpretation.[12] It is therefore of interest to determine the conditions of density and molecular eccentricity required to sustain nematic ordering. Such information should provide some insight into the question of which molecular systems may be expected to exhibit a nematic phase.

We have examined the stability of nematic ordering in a number of two dimensional systems of ellipses which differ in number density ρ and axial ratio $a = \sigma_\parallel/\sigma_\perp$. In a geometric interpretation of nematic ordering, the temperature would be expected to play a less important role than ρ or a. The temperature was consequently not treated as an independent variable. In each system, however, constant temperature was maintained by the velocity scaling technique common in molecular dynamics studies.

At the start of each run, rotational order was imposed by switching on an external electric field. Each of the 144 molecules was imagined to have an anisotropic polarizability of the form

$$\boldsymbol{\alpha} = \alpha_\parallel \hat{u}\hat{u} + \alpha_\perp(\mathbf{I} - \hat{u}\hat{u}) ,$$

where $\mathbf{I}$ is the unit tensor. In the presence of an electric field $\mathbf{E}$, a term is added to the energy of each molecule of the form

$$V_e = -\tfrac{1}{2}\mathbf{E}\cdot\boldsymbol{\alpha}\cdot\mathbf{E} .$$

If $\mathbf{E} = E\hat{n}$, where $\hat{n}$ is a space fixed direction, and $\alpha_\parallel > \alpha_\perp$, then V_e produces a torque tending to align the molecules along $\hat{n}$. Therefore, when the field is on the entire system becomes rotationally ordered. The degree of order is measured by a rotational order parameter ζ,

$$\zeta = \begin{cases} \langle(\hat{u}\cdot\hat{n})^2 - \frac{1}{2}\rangle \ ; & 2 \text{ dim} \\ \langle\frac{3}{2}(\hat{u}\cdot\hat{n})^2 - \frac{1}{2}\rangle \ ; & 3 \text{ dim} \end{cases}$$

where the average is taken over all the molecules in the system.

After a system is ordered by means of the electric field, the field is switched off. The order parameter ζ is then monitored to see whether the field-induced order relaxes. If the order parameter stabilizes at a value significantly higher than zero, and if the density of the system is lower than the expected solid density, we infer that the nematic phase exists.

There is a substantial difficulty with this procedure. One can never be certain that a given system has attained thermodynamic equilibrium.[13] It is easy to see that a very dense system may become caught in a configurational bottleneck, which results in a long lived metastable state. Indeed, we have noted, in several of our studies, time periods on the order of 10 000 time steps during which the order parameter did not vary systematically, followed by a sudden change of ζ to a new plateau value. Such a shift in the value of ζ indicates that the system has found a pathway to a persumably more stable configuration. Therefore, one must be guided to some degree by intuition and by past experience in the interpretation of these studies.

The results of our studies are summarized in Table

TABLE I. Results of studies on the stability of rotational ordering. a is the axial ratio, ρ/ρ_0 the density relative to the close packed density, M the number of time steps calculated, and ζ the final value of the rotational order parameter.

a	ρ/ρ_0	M	ζ
3	0.75	42 000	0.83
3	0.70	38 000	0.44
3	0.65	36 000	0.21
3	0.63	40 000	0.15
3	0.60	14 000	0.03
2	0.90	20 000	0.75
2	0.80	44 000	0.17

I. The density for each system is expressed relative to ρ_0, the density at close packing. ρ_0 is obtained by considering a system of hard spheres of diameter σ_0. In two dimensions the density at close packing for such a system is $\rho_0\sigma_0^2 = 2/\sqrt{3}$. For a system of ellipses of axes σ_0 and $a\sigma_0$ one obtains $\rho_0\sigma_0^2 = 2/a\sqrt{3}$. The column headed by M indicates the number of time steps for which each system was followed after the electric field was switched off. ζ is the approximate value of the rotational order parameter after the M steps. In the states of low rotational order ($\zeta < 0.3$), ζ was subject to fluctuations of large amplitude and extremely long lifetime (greater than 2000 steps). As a result, a reliable determination of ζ for these states was quite difficult.[14]

There has been a recent Monte Carlo study in two dimensions of the equation of state of ellipses of axial ratio 6.[15] In this study a solid–nematic transition was observed at a melting density of $\rho_m/\rho_0 = 0.87$. In addition, it is known that the melting density for hard discs ($a = 1$) is $\rho_m/\rho_0 = 0.79$.[16] It is therefore reasonable to assume that the melting densities for ellipses of $a = 2$ and $a = 3$ lie between these two values. We note from Table I that the state ($a = 3$, $\rho/\rho_0 = 0.75$) appears to have stable rotational ordering at a density below the expected solid density. Even at the still lower density $\rho/\rho_0 = 0.70$, the $a = 3$ system maintains significant ordering.

These results indicate that a system of ellipses of axial ratio 3 is capable of exhibiting a stable nematic phase in a range of densities intermediate between the solid and the isotropic liquid. This behavior is in contrast to the two dimensional $a = 2$ system. In the latter case, at density $\rho/\rho_0 = 0.80$, which should be very close to the melting density, the degree of rotational order is still quite low. The system seems well ordered at $\rho/\rho_0 = 0.90$, but such a high density should correspond to the solid phase.

The variation of ζ with ρ/ρ_0 for $a = 2$ and $a = 3$ is displayed in Fig. 1, along with the results of Ref. 15 for $a = 6$. The plots illustrate the loss of ability to sustain rotational order as the axial ratio is lowered.

In addition, we have carried out a number of studies of nematic stability in three dimensions. These studies were less systematic than the two dimensional studies described above, but a state was found which appears to support stable rotational ordering. This state, with $a = 3.5$, $\rho/\rho_0 = 0.71$, and $\zeta = 0.85$, was used as a prototype for nematic behavior in some of our previous work.[5,6] We have also used this state to observe anisotropic effects in translational self-diffusion.

A simple argument involving tensor analysis (see Appendix) may be used to relate ζ to $D_\parallel/D_\perp$, the ratio of the distinct principal components of the self-diffusion coefficient tensor.[17] The result of this argument is

$$\frac{D_\parallel}{D_\perp} = \frac{(1+2\zeta)(D_\parallel^0/D_\perp^0) + 2(1-\zeta)}{(1-\zeta)(D_\parallel^0/D_\perp^0) + (2+\zeta)} .$$

$D_\parallel^0/D_\perp^0$ is the ratio which would be observed in a system of perfect rotational alignment ($\zeta = 1$). If $D_\parallel/D_\perp$ is known for a particular ζ, the above expression may be used to find $D_\parallel/D_\perp$ for any ζ.

In Ref. 6 we have presented graphs of the velocity correlation function for our three dimensional nematic-like system, decomposed into velocity components parallel and perpendicular to the preferred alignment direction. (In these studies it is clear that an ellipsoid is more mobile when moving parallel to its principal axis than perpendicular to it. This conclusion is also reached with respect to translations in the isotropic liquid phase.) From the area under these curves, $D_\parallel/D_\perp$ was found to be 7.14. Since $\zeta = 0.85$ for this system, we may use our expression to estimate $D_\parallel/D_\perp$ for a model system with an order parameter typical of an actual nematic liquid crystal. It has been determined that $\zeta = 0.556$ for para-azoxyanisole (PAA) at 125 °C.[18] Our model would then predict $D_\parallel/D_\perp = 3.35$. This estimate is considerably above the recently measured value of 1.26.[19] Nevertheless, given the simplicity of our model, we regard the studies described here as quite useful in establishing a physical picture of how nematic anisotropy comes about, and in observing qualitatively the effects of this anisotropy.

COLLECTIVE EFFECTS IN REORIENTATION

It has been known for some time that depolarized light scattering may be used to probe the dynamics of molecular reorientation.[20] The line shape observed in Raman scattering contains information about single particle reorientation, while the Rayleigh scattering line shape may be influenced by cooperative rotational dynamics in the scattering volume. If the rotational width of a Lorentzian Raman line is Γ_s, then recent theoretical analysis has shown that the spectrum of collective reorientations is also characterized by a single width Γ_c which is simply related to Γ_s[21,22]:

$$\Gamma_c = \Gamma_s[(1+Ng)/(1+Nf)].$$

Here, N is the total number of scattering molecules in the scattering volume, and f is a factor describing the static orientational correlation of distinct molecules. For molecules with cylindrical symmetry, f is given by

$$f = \langle P_2(\hat{u}_i \cdot \hat{u}_j)\rangle ,$$

where $\hat{u}_i$ and $\hat{u}_j$ are the major axis vectors of two different scatterers. g measures the dynamic angular momentum correlation of two distinct molecules.

Recent experiments have been conducted to investigate

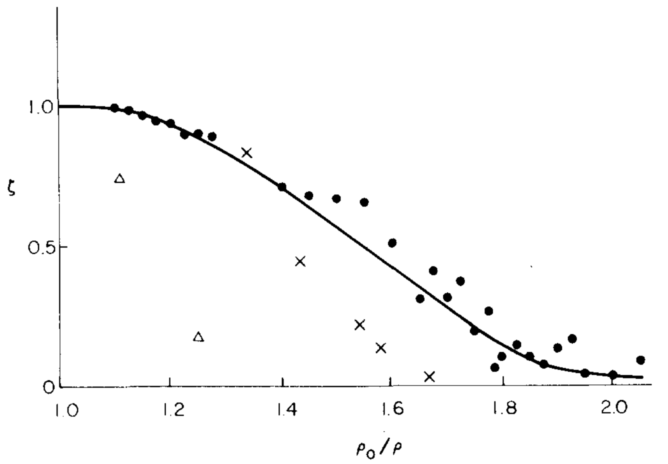

FIG. 2. The variation of the rotational order parameter with density. The dots and the curve going through them were taken from Ref. 15 for ellipses of axial ratio 6. The crosses are our data for $a=3$ and the triangles are our data for $a=2$.

the effect of cooperative rotation on depolarized Rayleigh line shapes.[23] We have examined these collective motions in two systems through molecular dynamics. One system consisted of 256 prolate ellipsoids with axial ratio $a=2$. The density was $\rho\sigma_0^3=0.405$ and the temperature was $kT/\epsilon_0=0.587$. In the other system, the particles were oblate ellipsoids modeled after the benzene molecule. The intermolecular potential parameters were selected to correspond to benzene by a numerical fit of the temperature dependence of the second virial coefficient.[24] The simulated density was 0.8787 g/cc, and the temperature was 80 °C. Both of these phase space trajectories were carried out for 3000 time steps.

The relevant single particle reorientation correlation function for cylindrically symmetric particles is $C_2(t)$:

$$C_2(t)=\langle P_2(\hat{u}(0)\cdot\hat{u}(t))\rangle .$$

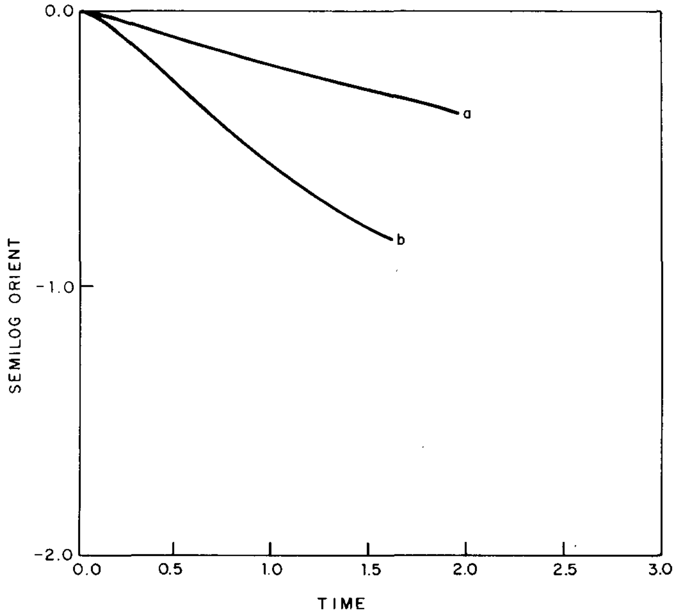

FIG. 3. $\text{Log}_{10}C_l(t)$ for system of prolate ellipsoids. (a) $l=1$, (b) $l=2$. The time is shown in reduced Lennard-Jones units of $\tau_0=\sigma_0(m/\epsilon_0)^{1/2}$.

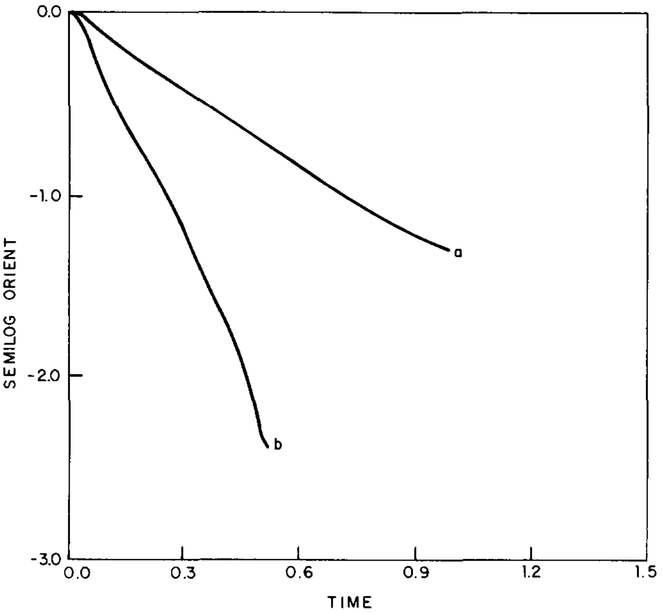

FIG. 4. $\text{Log}_{10}C_l(t)$ for benzene-like system. (a) $l=1$, (b) $l=2$. The time is shown in reduced Lennard-Jones units of $\tau_0=\sigma_0(m/\epsilon_0)^{1/2}$.

If a scattering volume contains N depolarizing scatterers, the relevant collective reorientation function is $C_2^N(t)$:

$$C_2^N(t)=\langle\sum_{i,j\in N}P_2(\hat{u}^i(0)\cdot\hat{u}^j(t))\rangle ,$$

where the particle indices i and j range among all of the N molecules. From our dynamics data, $C_2(t)$ was calculated in the normal manner for evaluating single particle correlation functions. To calculate $C_2^N(t)$, we labeled N of the 256 ellipsoids at random and only considered correlations among the labeled molecules. N could then be varied so that a sampling of "concentrations" of scatterers could be observed from a single molecular dynamics trajectory.

Figures 3 and 4 show the function $C_2(t)$ for the two dynamics systems, as well as the analogously defined reorientation correlation function $C_1(t)$. From the approximately linear shapes of the semilog plots, and from the ratios of the slopes ($\Gamma_2/\Gamma_1\approx 3$) of $C_2(t)$ and $C_1(t)$ for the two systems, one can see that these systems are fairly well described by the Debye model of rotational diffusion. Single particle rotational spectral line shapes for these systems would therefore be Lorentzians, with the width Γ_s related to the rotational diffusion coefficient.

The function $C_2^N(t)$ for a number of concentrations are shown in Figs. 5 and 6. In accord with theory, the cooperative reorientation correlation functions are each characterized by a single relaxation rate Γ_c. Collective effects manifest themselves primarily by decreasing Γ_c as the concentration increases. Our data was not sufficiently precise to permit a reliable quantitative determination of the variation of Γ_c with N. Nevertheless, our results provide a complement to the theory by illu-

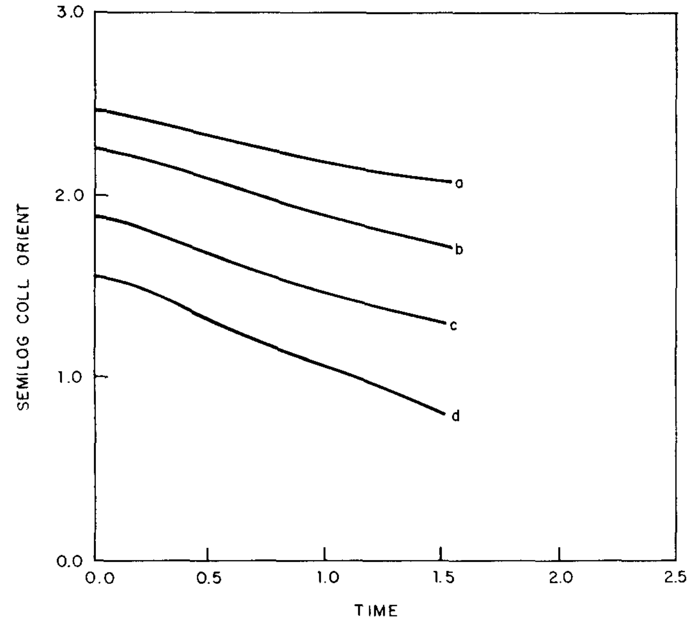

FIG. 5. $\log_{10} C_2^N(t)$ for system of prolate ellipsoids. (a) $N=192$, (b) $N=128$, (c) $N=64$, (d) $N=32$. The time is shown in reduced Lennard-Jones units of $\tau_0=\sigma_0(m/\epsilon_0)^{1/2}$.

strating the contribution of collective motion to rotational spectra.

DISCUSSION

In the molecular dynamics studies reported here the potential used was a Gaussian overlap model Lennard-Jones (12-6) potential truncated at its minimum. Several previous studies have shown that for sufficiently dense systems the truncation should not significantly alter the structure or dynamical behavior[25,6] of the fluid. As was already pointed out truncation results in a considerable saving of machine time. Despite this, these studies require a rather generous parcel of machine time—so much so, in fact, that it is very difficult to study the orientational properties of highly anisotropic fluids with sufficient accuracy to make definitive quantitative statements. One of the big problems results from the fact that there exist two widely different time scales typifying the translations and reorientations. In dense highly anisotropic systems the angular velocity decays very rapidly compared to the reorientations. Thus to examine orientational correlations one must generate a very long trajectory—a very costly procedure. Thus it is imperative to develop codes for handling systems with two widely different time scales. Some progress has been made in this context in a different problem, diffusion in the solid state. Nevertheless much remains to be done here. Also larger systems must be dealt with. Using modified bookkeeping procedures[26] we are currently studying considerably larger systems.

Given the foregoing difficulties, this article can only be considered as a "first foray" into the important area of anisotropic fluids. There are several novel procedures used in this study. To our knowledge this is the first time in molecular dynamics that any orientationally ordered phase has been studied. This was accomplished by subjecting the disordered fluid to an orienting (symmetry breaking) external field. When this external field is turned off the system either retains its order or does not. The time dependence of this order parameter was determined. The main feature to be stressed here is that there should be many applications in molecular dynamics in which ordering fields will be useful.

It should be noted that we have simulated only pure fluids. Nevertheless, by randomly labeling particles we have been able to study the cooperative properties of solutions. This technique should be of considerable utility in solution studies. Of course it is possible to simulate solutions consisting of entirely different molecules. This however is a very time consuming and expensive task. At low concentrations very lengthy run times are required to obtain useful statistics. In addition each concentration requires an entirely new run. Of course this lengthy program is desirable for studying real solutions. Our technique however is very useful for the study of a fictitiously labeled solution. In one production run it is possible to study solutions over a wide range of concentrations by simply sampling different numbers of labels.

As far as our model potentials are concerned, they are simple, intuitively appealing, and quite analogous to those model potentials that have served the statistical mechanics community so well in the past. Recently MacRury *et al.* have determined the potential parameters for several molecules from gas phase virial coefficients and have compared this model to other potential models.[24] The usefulness of the model is demonstrated.

Needless to say, much remains to be done with these interesting systems. This paper should be regarded as the first in a series of studies on anisotropic fluids.

APPENDIX

In this Appendix, we derive the relation between $D_\parallel/D_\perp$ and ζ used in the text. Consider an "ideal" nematic sample which is perfectly aligned; that is, all of the molecular $\hat{u}$'s are the same direction. A general expression for the diffusion tensor of this material is

$$\mathbf{D}^0 = D_0^0\,\mathbf{I} + (D_\parallel^0 - D_\perp^0)(\hat{u}\hat{u} - \tfrac{1}{3}\,\mathbf{I}) \;,$$

where $D_0^0 = \frac{1}{3}(D_\parallel^0 + 2D_\perp^0)$. The diffusion tensor of a real nematic may then be written as an average over the distribution of molecular $\hat{u}$'s:

$$\mathbf{D} = D_0^0\,\mathbf{I} + (D_\parallel^0 - D_\perp^0)\langle\hat{u}\hat{u} - \tfrac{1}{3}\,\mathbf{I}\rangle \;.$$

If the preferred alignment direction is $\hat{n}$, the component of $\mathbf{D}$ describing diffusion parallel to $\hat{n}$ is

$$D_\parallel = \hat{n}\cdot\mathbf{D}\cdot\hat{n} = D_0^0 + (D_\parallel^0 - D_\perp^0)\langle(\hat{u}\cdot\hat{n})^2 - \tfrac{1}{3}\rangle \;.$$

Since the rotational order parameter has been defined by

$$\zeta = \langle P_2(\hat{u}\cdot\hat{n})\rangle \;,$$

we obtain

$$D_\parallel = D_0^0 + \tfrac{2}{3}\,(D_\parallel^0 - D_\perp^0)\,\zeta \;.$$

Now, molecular rotation can not alter the trace of $\mathbf{D}$. The component of $\mathbf{D}$ describing diffusion perpendicular to $\hat{n}$, $D_\perp$, may therefore be obtained from

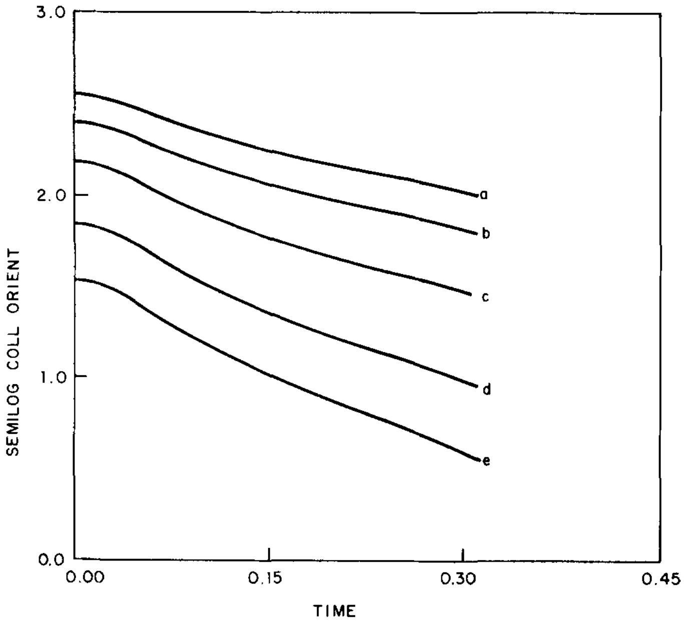

FIG. 6. $\mathrm{Log}_{10}C_2^N(t)$ for benzene-like system. (a) $N=256$, (b) $N=192$, (c) $N=128$, (d) $N=64$, (e) $N=32$. The time is shown in reduced Lennard-Jones units of $\tau_0=\sigma_0(m/\epsilon_0)^{1/2}$.

$$D_\parallel + 2D_\perp = D_\parallel^0 + 2D_\perp^0 = 3D_0^0 \; .$$

The result is

$$D_\perp = D_0^0 - \tfrac{1}{3}(D_\parallel^0 - D_\perp^0)\,\zeta \; .$$

The above expressions for $D_\parallel$ and $D_\perp$ may be rearranged and combined to yield

$$\frac{D_\parallel}{D_\perp} = \frac{(1+2\zeta)(D_\parallel^0/D_\perp^0)+2(1-\zeta)}{(1-\zeta)(D_\parallel^0/D_\perp^0)+(2+\zeta)} \; .$$

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[†] Present address: James Franck Institute, University of Chicago, Chicago, IL 60637.

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