COMPUTER SIMULATION OF MOLECULAR ORIENTATIONAL ORDER: THE KERR EFFECT IN CARBON DISULPHIDE

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We have performed a molecular dynamics computer simulation on the liquid state of the linear triatomic molecule, carbon disulphide. On the time-scale of a few picoseconds, the reorientation of these molecules in response to an external electric field has been followed explicitly. The failure of a classical orientational diffusion model to reproduce the results of the simulation is observed for high fields. A simple modification of the diffusion model is found to restore most of its qualitative predictive power.

1. Introduction

In its simplest form, the Kerr effect describes the process whereby nonspherical molecules in a liquid are oriented by an applied electric field. Among the simplest readily available Kerr liquids is the linear triatomic molecular liquid CS$_2$. Unlike its more prevalent counterpart, CO$_2$, it is a liquid at room temperature and hence a convenient system in which to study dynamics and statics of molecular fluids.

Because of p$_1$-electron bonding, CS$_2$ has a rather large anisotropic molecular polarizability and because of its symmetry it has no ground state dipole moment. Although large aromatic molecules have much larger anisotropies in their polarizabilities, the physical size of long molecules causes their reorientation in an applied field to occur over a long time scale. A short time interval in liquids is one near the collision time. Characteristic times around $10^{-12}$ seconds are typical of room temperature liquids. Experimental measurements assign an orientational relaxation time of about $2 \text{ psec}$ to CS$_2$, hence the liquid exists in a regime where orientational processes compete with collisional relaxation processes, and classical ideas of orientational viscosity lose their appeal.

In this study, we will use molecular dynamics to investigate where the breakdown of classical diffusion models occurs. We wish to determine if this is a qualitative or quantitative problem, and to elucidate the extent to which a repair of the classical theory may be affected in a simple way.

2. The Model Liquid

The carbon disulphide molecule is composed of a linear arrangement of sulfur-carbon-sulfur atoms. The bond length between the sulfur and carbon is measured to be $1.57 \, \text{Å}$. Previous studies of the equilibrium static and dynamic properties of this liquid have found that the intermolecular interactions of CS$_2$ molecules are reasonably well approximated by a sum of pair-wise atomic Lennard-Jones interactions. Furthermore, the rigidity of the linear molecule seems to allow the use of a model where the molecule is strictly linear with a fixed (rigid) bond length. We have adopted the same model parameters as used by previous investigators for the same reasons which lead them to their choices. The liquid state thermodynamic properties are reproduced with an accuracy considered comparable to rare gas atomic systems. Including high frequency bending and vibrational motion is almost certainly an unwarranted computational expense. For the very reasonable arguments supporting these assertions, we refer the reader to the earlier works on equilibrium properties of molecular liquids by other authors.

The carbon-disulphide molecular interaction parameters which we have employed are:

$$
\epsilon_{SS}/k = 183.0 \, ^\circ K \quad \sigma_{SS} = 3.52 \, \text{Å} \\
\epsilon_{CC}/k = 51.2 \, ^\circ K \quad \sigma_{CC} = 3.35 \, \text{Å} \\
\epsilon_{CS}/k = 96.8 \, ^\circ K \quad \sigma_{SC} = 3.44 \, \text{Å}
$$

The equilibrium density varies somewhat among different investigators, but we have used $\rho_0 = 0.32422$ where $\sigma = \sigma_{CC}$ and $\rho$ is the number density of molecules. The temperature of the liquid under investigation changes with time due to the transfer of energy from the applied field, but we will uniformly begin the dynamical simulations with a fluid at $395^\circ \text{K}$ unless specifically noted otherwise.

3. The Hamiltonian and Equations of Motion

The results which we report are for 500 particles in a fixed periodic volume determined...
molecular orientations are uniformly randomly distributed. The pair correlations are, however, not random, and as one might expect at short intermolecular separations, but are randomly distributed when the separation distances exceed several molecular lengths. These correlations are manifested in an orientational correlation function

\[ \langle \hat{m}(0) \cdot \hat{m}(r) \rangle \]

which is the average of the second Legendre polynomial of the cosine of the angle between molecular orientations \( \hat{m} \) at a separation distance \( r \). This correlation function is shown in Figure 1, and illustrates quantitatively the spatial decay of orientational pair correlations with separation distance. The results in Figure 1 also illustrate that the size of the simulation volume needs to be large enough so that these correlations nearly vanish over a distance which is less than half the length of the side of the simulation cube. For values of \( r \) less than the size of the simulation volume, we anticipate testing this conjecture in the future however.

4. Static Properties

In the absence of an applied field, the molecular orientations are uniformly randomly distributed. The potential energy \( u \) of the molecule due to the external field is then

\[ u = -\frac{1}{2} \alpha \cdot \nabla \cdot \nabla \cdot \nabla \]

The resulting torque has the magnitude

\[ \tau = \frac{\Delta \alpha}{2} E^2 \sin 2\theta, \]

where \( \theta \) is the angle between the field direction and the axis of symmetry of the molecule. The anisotropy of the molecular polarizability, \( \Delta \alpha \), is the difference in the polarizability in the directions parallel and perpendicular to the molecular symmetry axis.

The most immediate effect of the induced dipole moment \( i \) is to cause a torque which tends to align the molecules with the external field. The dipole-moment vectors have not been included in this study. We believe that the "collisional" relaxation processes dominate the dynamics of reorientation and we do not expect qualitative changes in the reorientational response of the liquid due to these induced intermolecular dipole interactions. We anticipate testing this conjecture in the future however.

\[ F = \Delta \alpha E^2 / 2k \]

is the appropriate measure of the strength of the applied field in \( \text{K} \). This measure also has the advantage of not requiring a specific value for the anisotropic molecular polarizability, since it only occurs in combination with the applied field. Experimental measurements would assign a value near \( 10.0 \times 10^{-24} \text{cm}^3 \) to this anisotropy.

Also plotted in Figure 2 are the predictions of the simple Lorentz model for the induced orientational order. This model predicts the orientation distribution will be determined simply by the Boltzmann factor

\[ \exp(-\Delta \alpha (\hat{m} \cdot E)^2 / 2kT). \]

This model completely neglects intermolecular interactions except inasmuch as collisions are recognized as the mechanism for thermalization. The remarkable feature of the comparison of these two predictions is in their agreement.

At higher temperatures and lower densities, in a regime where orientational pair correlations decay on the scale of one molecular length, one expects the premises of the simple theory to be valid and hence expects agreement with simulation results. At liquid densities near room temperature, orientational correlations are not short ranged and the reasons for the validity of the simple Lorentz model are obscure. One expects that it must fail at higher density/
The time evolution of the orientational order in the molecular dynamics simulation was monitored by calculating \( \langle p_2(\mathbf{h}(t) \cdot \mathbf{z}) \rangle \) which is proportional to

\[
D \frac{\partial^2 \rho}{\partial t^2} + \frac{D}{kT} \nabla \cdot (\rho \nabla V(\theta)) = \frac{3\rho}{\partial t}(\theta, t) \tag{1}
\]

Here \( \rho(\theta, t) \) is the probability that a molecule will be found at an orientation \( \theta \) of time \( t \) and \( V(\theta) \) is the potential energy of a molecule at angle \( \theta \). The gradient \( \nabla \) contains only angular variables. \( D \) is a rotational diffusion constant.

We have specialized to the case of axially symmetric molecules in a uniform field, hence there is no dependence on the azimuthal angle \( \phi \) in the equation. The equilibrium, \( t \rightarrow \infty \), solution to this equation is readily shown to be the Boltzmann distribution. Unlike the static case, the premises of the simple diffusion theory suggest that the regime of validity of this model is high density (many collisions) and moderate temperature (slow rotation).

Furthermore, a large length to breadth ratio of molecular dimensions implies hindered rotation due to collisions. When these conditions are substantially violated, one expects the diffusion model to fail. In particular, if the collision frequency is low, inertial effects may enter.

This diffusion model has been used by Watanabe\(^7\) to study the orientational response of a molecular liquid to various applied fields. The details of our method of solving the diffusion equation will be omitted in favor of a brief summary. For any time \( t \), the density \( \rho(\theta, t) \) may be expanded in Legendre polynomials

\[
\rho(\theta, t) = \sum_{n=0}^{\infty} a_n(t) P_n(\cos \theta).
\]

The normalization is fixed by \( a_0 = 1/4\pi \) for all times. Substituting this expansion into the diffusion equation leads to a set of coupled first order differential equations in time for the coefficients \( a_n(t) \). The initial conditions are given by the values \( a_n(0) \). For an initially isotropic liquid \( a_n(0) = 0 \) for \( n \neq 0 \). The symmetry of our present problem insures that terms with \( n \) odd are identically zero. The solution for \( a_n(t) \) is achieved by a Runge-Kutta integration of the differential equations. A second set of solutions which were investigated is the time evolution of a system initially in equilibrium in a constant field which is switched off at \( t=0 \). In this case, the initial conditions for the \( a_n(0) \) are determined from the Boltzmann distribution. The solutions are analytically known in the absence of a field are,

\[
a_n(t) = a_n(0) e^{-n(n+1)D t}.
\]

The time evolution of the orientational order in the molecular dynamics simulation was monitored by calculating \( a_2(t) \) which is proportional to

\[
\langle p_2(\mathbf{h}(t) \cdot \mathbf{z}) \rangle
\]

The value of this order parameter is zero for an isotropic system and unity for a perfectly orientationally ordered fluid. The field
direction was arbitrarily chosen in the \( \hat{z} \)-direction.

We first considered the response of the isotropic fluid to a constant external field. The time evolution of the induced orientational order is shown in Figure 3 for two different field strengths. The induced orientation shows the rather simple monotonic growth behavior which one expects from the diffusion arguments presented earlier. Even with 500 molecules, there is a certain amount of fluctuation in the quantity \( \langle P_2(m(t)\cdot \hat{z}) \rangle \) from run to run. One expects this since, at any given instant in time, even the isotropic fluid of 500 molecules will not have exactly zero orientational order. This is presumably the same type of local order fluctuations that exist even in an infinite fluid. The results shown in Figure 3 are the average of five different simulations from five different isotropic equilibrium configurations. The "wiggles" which remain in the molecular dynamics curves in Figure 3 are almost certainly manifestations of these fluctuations and would probably diminish if more runs were averaged. Thus for this molecular fluid we see smooth monotonic increases in molecular order due to the applied field and no inertial effects seem to be manifested.

The interesting aspect of the comparison of the results of the solution of the diffusion equation and the molecular dynamics results is that they agree well for small field strengths and disagree for large field strengths. The reason for this becomes apparent when one observes that the temperature of the fluid increases with time in the molecular dynamics calculations. At \( t=0 \), the application of a field to the isotropic fluid puts the system into an initial nonequilibrium state of high potential energy. As time evolves, the potential energy is transformed to kinetic energy as the system approaches the equilibrium state with a net molecular orientational order. Since the molecular dynamics calculation is energy conserving, the increase in kinetic energy shows up as an increase in temperature. Since this entire process occurs over a few picoseconds, a laboratory system would also be described as a constant energy rather than constant temperature ensemble average. We argue, therefore, that the molecular dynamics results are appropriate to compare with experimental results and the diffusion equation at constant temperature fails at high field strengths.

The above analysis suggests that a simple change be made in the diffusion equation to recognize that the temperature is time dependent. One would like to avoid as many arbitrary constants as possible and retain the classical diffusion model with just the one phenomenological parameter, the diffusion constant.

The potential energy of the system due to the external field is given by

\[
PE_x(t) = \int d\theta \, v(\theta) \rho(\theta,t).
\]

(4)

This neglects any changes in potential energy due to intermolecular interactions, but since the diffusion equation ignores these details, it is consistent with that approximation to ignore them in calculating changes in \( PE_x \). To make the diffusion equation satisfy a constant energy constraint, one requires that the kinetic energy vary in time in such a way that

![Fig. 3](image-url)  
**Fig. 3** Induced orientational order as a function of time after applied field. Upper curves are field strength

\( F=3950 \text{ K} \), lower curves \( F=395 \text{ K} \). Symbols are: \( \bigcirc \) molecular dynamics, *** diffusion equation, — modified diffusion equation.

![Fig. 4](image-url)  
**Fig. 4** Temperature increase as a function of time after a field is applied. Solid curves are from the modified diffusion equation. Symbols are molecular dynamic results. Field strengths are \( F=1975 \text{ K} \), \( 1185 \text{ K} \), and \( 790 \text{ K} \) from top to bottom.
Then the temperature has a time dependence of

\[ \frac{5}{2} kT(t) = KE(t). \]  

(6)

This assumes two other things, firstly, the diffusion constant is temperature independent, and the change in kinetic energy is distributed equally between each rotational and translational degree of freedom. These seemingly serious assumptions yield, in our view, an obvious consistent and simple change in the diffusion equation.

Solving the diffusion equation through a Runge-Kutta integration scheme is as simple with time dependence in the temperature as it was without it. The asymptotic solution is still given by a Boltzmann distribution but at a higher temperature. The time dependence of the temperature of the fluid in an external field as predicted by the constant energy diffusion equation and as calculated by molecular dynamics is shown in Figure 4. Within the uncertainty of the molecular dynamics results, this figure shows surprisingly accurate agreement. The total time dependence of the order as predicted by the constant energy diffusion equation is now shown in Figure 3. The time dependence is then seen to be in agreement with molecular dynamics as well.

6. Conclusions

We did not expect the kind of agreement which was found between molecular dynamics and the energy conserving diffusion equation. It would appear that all the qualitative characteristics are reproduced properly and to within 10%, quantitative agreement is found over a wide range of field strengths. Only one phenomenological diffusion constant of \( D \approx 0.2 \times 10^{12} \) sec was used in all the fits.

As indicated earlier, further computer simulations of these molecular liquids studying their responses to applied fields are planned. Although testing classical diffusion models is not the motivation of this work, it will be interesting to determine if they continue to work well under other physically relevant conditions.

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