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# Models of Diffusion in Lyotropic Liquid Crystals

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The asymmetric diffusion of small molecules in a liquid crystal host is examined via three models. The small molecules are represented by spheres and the liquid crystal host by aligned cylinders. DASH is a continuum model which allows one to use the results of electrical conductivity problems to calculate the diffusion coefficient. LASH is an extension of polymer lattice counting models. CASH is a molecular dynamics computer simulation which provides experimental data to check the analytical models. It is found that DASH is a better representation of the diffusion asymmetry than LASH for the low liquid crystal densities examined on the computer. The cylinder sphere pair correlation function is also calculated in CASH and this gives evidence for liquid order around the liquid crystals.

## INTRODUCTION

Recently, liquid crystals have become a focal point of intense scientific study<sup>1</sup> because of their biological and technological importance. These materials are substances intermediate in properties between isotropic random liquids and ordered solids; for example, they behave like liquids mechanically but like solids optically. This behavior is caused by the existence of a partial directional order in the long axes of molecules forming liquid crystals. This order implies an asymmetry in properties such as viscosity and diffusion, since flow will be much less hindered parallel to the direction of the unique liquid crystal axis than perpendicular to it. There are two basic types of liquid crystals: lyotropic and

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thermotropic. Lyotropic liquid crystals are formed by mixing large, asymmetric solutes with small, symmetric solvents; e.g. poly- $\gamma$ -benzyl-L-glutamate with dioxan. Thermotropic liquid crystals are formed by heating a pure, asymmetric material; e.g. p-azoxyanisole. Here, we examine diffusion in lyotropic liquid crystals; Kushich and Berne<sup>2</sup> are investigating diffusion in thermotropic materials. Three separate models are examined in this study: DASH, LASH and CASH. The acronyms represent the diffusion analogue simulated habitat, the lattice analogue simulated habitat, and the computer analogue simulated habitat. These models are discussed in the following three sections and then compared in Sect. V. In the appendix the asymmetric diffusion of the LASH model is expressed in terms of the order parameter.

### THE DIFFUSION EQUATION APPROACH TO LIQUID CRYSTAL DIFFUSION (DASH)

The first model for which the asymmetric diffusion coefficient will be computed consists of a solution of large non-flexible molecules and solvent. The model applies to molecules of any shape but for simplicity we shall always use cylinders. It is postulated that these molecules do not move much during the self-diffusion of the solvent molecules. The diffusion of solvent is held to obey the following Fickian diffusion laws:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \text{ (in the interior between cylinders)} \quad \text{II (1a)}$$

$$\nabla C|_n = 0 \text{ (on the cylinder walls)} \quad \text{II (1b)}$$

$$\mathbf{J} = -D \nabla C \quad \text{II (1c)}$$

where  $C$  is the concentration,  $\mathbf{J}$  is the current, and  $D$  is the diffusion coefficient. If one were concerned with diffusion in the small, that is to say over distances comparable to the average separation between cylinders, then the problem would be especially difficult. However, if one is content to discuss diffusion over distances large compared to the separation between cylinders the problem can be simplified. Consider a region of the material. If the concentrations on the boundaries were constant then the current  $\mathbf{J}$  could be determined as a steady state solution. We can show that this limit is closely approximated when the concentration gradient changes slowly. For simplicity we illustrate this for the one dimensional case with a region of length  $\Delta X$ .

In order for steady state conditions to be valid the rate,  $\mathbf{J}$ , at which material flows through the region must be large compared to the rate of accumulation of material within the region,  $\partial(\Delta XC)/\partial t$ .

Hence,

$$\frac{\frac{\partial (\Delta X C)}{\partial t}}{J} = \frac{\Delta X \frac{\partial^2 C}{\partial X^2}}{\frac{\partial C}{\partial X}} \ll 1 \quad \text{II (2)}$$

Eq. (2) can always be made to hold for long times because the Gaussianlike distribution broadens enormously with time. We are interested in using the steady state approximation for distances which encompass many cylinders. The equation

$$\Delta X \frac{\partial^2 C}{\partial X^2} / \frac{\partial C}{\partial X} = 1 \quad \text{II (3)}$$

can be used to define a  $\Delta X$  which may be compared to the average separation,  $d$ , between cylinders. Clearly for the case

$$d \frac{\partial^2 C}{\partial X^2} / \frac{\partial C}{\partial X} \ll 1 \quad \text{II (4)}$$

the steady state condition applies. When the concentration gradient changes sufficiently slowly,  $\frac{\partial^2 C}{\partial X^2}$  will be sufficiently small for Eq. II(4) to be satisfied.

When the corresponding three dimensional steady state condition is valid, Eq. (1) reduces to

$$\begin{aligned} 0 &= \nabla^2 C; \quad \nabla C|_n = 0 \\ J &= -D \nabla C \end{aligned} \quad \text{II (5)}$$

Observe that Eq. (5) is identical to the problem of electric current flow in a conductive medium (solution) in which are imbedded insulated regions (large molecules):

$$\begin{aligned} \nabla \cdot j &= 0 \quad j|_n = 0 \\ j &= \sigma \nabla V \end{aligned} \quad \text{II (6)}$$

where  $V$  is the potential,  $\sigma$  the conductivity, and  $j$  the current density. Thus, the problem of calculating  $D$  is identical to the problem of calculating the conductivity of a composite material. This analogy is useful for two reasons. First many computations have been made on the conductivity problem and their results can be taken over bodily. Second, for systems too complicated to solve analytically one can actually make electrical resistivity measurements on the electrical analogue of the liquid crystal system<sup>3</sup>.

We would like to show that  $D$  is a second-order tensor by consideration of

the electrical analogue. This can be done in two steps. First, observe that the power dissipation in the principal axes coordinates is

$$P = \sum \sigma_i E_i^2 \quad \text{II (7)}$$

where  $E_i$  is the electric field and  $\sigma_i$  is the conductivity in the  $i$ th direction. In this reference frame the current,  $J_i = \sigma_i E_i$ , lies in the same direction as  $E_i$ . Second, since  $\mathbf{E}$  is a vector and  $P$  an invariant,  $\sigma_i$  must be a tensor by the quotient law of tensor calculus<sup>4</sup>. That is to say, in an orthogonal coordinate system rotated arbitrarily with respect to the principal axes, we have

$$P = \sum_{i,j} \sigma_{ij} E_i E_j \quad \text{II (8)}$$

The diffusion coefficient,  $D_{ij}$ , will now be calculated for the same model on which we will do computer simulations. This is a random array of very long parallel rigid rods (cylinders). The diffusion of material along the direction of the rods is a one dimensional problem and is determined by solving the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \quad \text{II (9)}$$

where  $D$  is the solvent diffusion coefficient. If we define an average concentration,  $\langle C \rangle$  which includes averaging over the total volume including the cylinders, then

$$\langle C \rangle = V_0 C \quad \text{II (10)}$$

because there is no material inside the cylinders. Here  $V_0$  is the volume fraction of solvent. It should be observed that definition II(10) means that  $\langle C \rangle$ , can be discontinuous; e.g. at the boundary between a liquid crystal and pure solvent. The current,  $\langle j \rangle$  is

$$\langle j \rangle = -D_{\parallel} \nabla \langle C \rangle = -D_{\parallel} \nabla (V_0 C) \quad \text{II (11)}$$

where  $D_{\parallel}$  is the diffusion coefficient parallel to the rods and for consistency  $\langle j \rangle$  is integrated over an area which includes the cylinders. But the equation of continuity gives

$$\frac{\partial C}{\partial t} + \nabla \cdot \langle j \rangle = 0 \quad \text{II (12)}$$

or

$$\frac{\partial \langle C \rangle}{\partial t} = D_{\parallel} \nabla^2 \langle C \rangle \quad \text{II (13)}$$

Substituting for  $\langle C \rangle$  we obtain

$$\frac{\partial C}{\partial t} = D_{\parallel} \nabla^2 C \quad \text{II (14)}$$

which when compared to Eq. (9) shows that

$$D_{\parallel} = D \quad \text{II (15)}$$

Thus, the concentration broadening of a slug of material proceeds according to the formula

$$\langle C \rangle = V_0 C = \frac{V_0 \exp(-X^2/2Dt)}{(4\pi Dt)^{1/2}} \quad \text{II (16)}$$

Were the formula for  $D_{\parallel}$  given by  $D = V_0 D$  as some suppose<sup>5</sup> the broadening would proceed at a different rate ( $2V_0 D$  instead of  $2D$ ).

The calculation of  $D_{\perp}$  is a little more difficult. This problem is equivalent to the two dimensional problem of conductivity in a plate which has holes punched in it randomly. The random placement of holes makes the problem impossible to solve analytically. We therefore replace this problem by one with a regular array of holes. The conductivity of these two geometries are expected not to differ much since the diffusion equation is parabolic. Were the diffusion equation hyperbolic in nature one could expect interference effects; scattering from the regular array would be much different than scattering from a random array. Now the problem of the conductivity of a conductive plate with a regular square array of non-conductive holes has been solved by Raleigh.<sup>6</sup> His result, obtained by solving the problem of a periodically replicated square with a single hole, is

$$\sigma_{\perp} = \sigma \left( 1 - \frac{2V_r}{1 + V_r - 0.305 V_r^4} \right) \quad \text{II (17)}$$

$$V_r = (1 - V_0)$$

where  $V_0$  is the volume fraction of solvent and  $V_r$  is the volume fraction of rods.

The corresponding material diffusion problem gives

$$\langle j \rangle = D \left( 1 - \frac{2V_r}{1 + V_r - 0.305 V_r^4} \right) \frac{\partial C}{\partial X} \quad \text{II (18)}$$

where  $j$  is the average current and  $C$  is the local concentration. In terms of the average quantities used before

$$\langle j \rangle = \frac{D}{V_0} \left( 1 - \frac{2V_r}{1 + V_r - 0.305 V_r^4} \right) \frac{\partial \langle C \rangle}{\partial X} \quad \text{II (19)}$$

$$\langle C \rangle = V_0 C$$

This equation plus the continuity equation

$$\frac{\partial \langle C \rangle}{\partial t} + \nabla \cdot \langle j \rangle = 0 \quad \text{II (20)}$$

yields

$$\frac{\partial \langle C \rangle}{\partial t} = D_{\perp} \frac{\partial^2 \langle C \rangle}{\partial X^2} \quad \text{II (21)}$$

$$D_{\perp} = \frac{D}{V_0} \left( 1 - \frac{2V_r}{1 + V_r - 0.305 V_r^4} \right) \quad \text{II (22)}$$

Since Raleigh's early work on electrical conductivity others have investigated the properties of composite materials and have obtained relationships between the transport properties of the composite and those of the continuous and dispersed phases.<sup>5</sup> These equations are useful for the study of processes such as heat conduction and mass diffusion as well as electrical conductivity. Nielson<sup>5</sup> reports the following empirical equations:

$$\frac{K}{K_0} = \frac{1 + ABV_r}{1 - BCV_r} \quad \text{II (23a)}$$

$$B = \frac{K_r - K_0}{K_r + K_0 A} \quad \text{II (23b)}$$

$$C = 1 + \left( \frac{1 - V_m}{V_m^2} \right) V_r \quad \text{II (23c)}$$

Here  $K$  is the property of interest of the two phase material, subscripts 0 and  $r$  refer to the continuous and dispersed phases, respectively,  $A$  is a constant which depends upon the shape of the dispersed particles and how they are oriented with respect to the direction of current flow, and  $V_m$  is the maximum packing fraction of the dispersed particles. Values of  $A$  and  $V_m$  are listed in Nielson's tables. When the dispersed particles are uniaxially oriented perpendicular to the current flow,  $A$  equals 0.5. When the closed packing configuration is a simple cubic array,  $V_m$  equals 0.785. Nielson's equations give

$$D_{\perp} = \frac{D}{V_0} \left[ \frac{1 - V_r}{1 + 2C V_r} \right] \quad \text{II (24a)}$$

$$C = 1 + 0.35 V_r \quad \text{II (24b)}$$

An interesting feature of these equations is that the absolute diameter of the rods is unimportant. This is a general feature of Eq. II(5);  $D$  is invariant to a scaling of the size of the rods. This agrees with the experimental measurements made by Barrer *et al.*<sup>3</sup> Furthermore, they found that conductive paper with random and regular arrays of holes had, within experimental limits, the same conductivity.

### A DISCRETE LATTICE MODEL APPROACH TO THE DIFFUSION COEFFICIENT (LASH)

The approach of the previous section has a severe limitation. The mean free path of the diffusing particle must be small compared to the diameter of the rigid rods. Moreover, the DASH model is a continuous model in which the size of the diffusing molecule is assumed to be small compared to the diameter of the solute molecules. We can supplement the previous method by one in which both the length of the diffusing step is equal to the size of the solute molecules and the size of the solvent particles is equal to the diameter of the solute molecule.

Our model will be a lattice model. Let us envisage a cubic lattice in which each cylinder is represented by  $r$  contiguous occupied sites in the  $Z$  direction and each solvent molecule is represented by one occupied site. Empty lattice sites are allowed. We will again assume that the solute molecules are fixed and attempt to calculate the self-diffusion coefficients of the solvent molecules. The solvent molecules are allowed to move only along each of the three mutually perpendicular bond directions. Also only jumps to adjacent empty sites are allowed. The length of a jump is the length of a bond. Under these conditions it is evident that the diffusion coefficient in a particular direction is proportional to the number of solvent hole pairs in that direction. In mathematical form

$$D_i \propto f_i(S, H) \quad \text{III (1)}$$

where  $f_i(S, H)$  is essentially the number of solvent hole pairs connected by a bond in the  $i$ th orientation and  $S$  and  $H$  represent solvent and hole sites respectively. Now the useful feature of Eq. (1) is that the quantity  $f_i(S, H)$  is easily calculated by methods already in the literature.<sup>7</sup> We must first convince ourselves that:

$$\frac{f_i(S, H)}{f_i(S, S)} = \frac{f_j(S, H)}{f_j(S, S)} \quad \text{III (2)}$$

Equation (2) is valid because the number of ways to pack solvent and polymer in the absence of the holes,  $W(P, S')$  is simply related to the number of ways to pack solvent, polymer and holes,  $W(P, S, H)$ .

$$W(P, S, H) = \frac{(N_S + N_H)!}{N_S! N_H!} W(P, S') \quad \text{III (3)}$$

$$N_S + N_H = N'_S$$

where  $N_S$  and  $N_H$  are the number of solvent molecules and holes respectively. That is to say, the only difference in the statistics is an entropy of mixing term for mixing solvent and holes which is not orientation dependent. Thus, if we know the statistics for solvent and polymer, then we also know it for solvent, polymer and holes. Therefore



$$D_i \propto f_i(S, S) \quad \text{III (4)}$$

Equation (4) can also be viewed directly as an ansatz for diffusion.

The probability of finding  $S$ - $S$  pairs in each of the various directions has been calculated previously.<sup>7</sup> Here we rederive the result for the special case of  $N_r$  rods of length  $r$  aligned in the  $Z$ -direction and  $N_o$  solvent molecules. Consider motion parallel to the rods. The probability of success of finding an adjacent solvent particle in the  $Z$ -direction ( $P_S$ ) is proportional to  $N_o$  whereas the probability of success of finding an adjacent rod in the  $Z$  direction ( $P_R$ ) is proportional to  $N_r$ . Since  $P_S + P_R = 1$ , one finds that

$$P_S = \frac{N_o}{N_o + N_r} \quad \text{III (5)}$$

If this expression is divided by the total number of filled sites  $N_o + rN_r$ , we obtain

$$P_S = \frac{V'_0}{1 - V'_r \left[ 1 - \frac{1}{r} \right]} \quad \text{III (6)}$$

where  $V'_0$  is the fraction of solvent ( $N_o/(N_o + rN_r)$ ) and  $V'_r$  is the fraction of rods ( $rN_r/(N_o + rN_r)$ ). Now consider motion perpendicular to the rods.  $P_s$  is still proportional to  $N_o$  but now  $P_R$  is proportional to  $rN_r$ . Therefore,

$$P_s = \frac{N_o}{N_o + rN_r} = V'_0 \quad \text{III (7)}$$

Thus, the diffusion coefficient components are

$$D_z = \frac{V'_0 D}{1 - V'_r \left( 1 - \frac{1}{r} \right)} \quad \text{III (8)}$$

$$D_x = D_y = V'_0 D$$

where  $D$  is the diffusion coefficient at zero concentration of  $r$ -mers. This formula can be generalized to the case where only a fraction  $\alpha$  of the molecules point in the direction  $z$  and  $[(1 - \alpha)/2]$  lie in directions  $x$  and  $y$ .

$$D_z = \frac{D V'_0}{1 - \alpha V'_r \left( 1 - \frac{1}{r} \right)}, \quad D_x = D_y = \frac{D V'_0}{1 - \left( \frac{1 - \alpha}{2} \right) V'_r \left( 1 - \frac{1}{r} \right)} \quad \text{III (9)}$$

These expressions may be further generalized to handle the situation in which the molecules are semi-flexible rather than stiff. Such results might be useful for

predicting the asymmetric diffusion coefficient in a stretched rubber. It has been pointed out in a previous paper<sup>8</sup> that probabilities are a function only of  $\alpha$  and not on the specific way these  $\alpha$  bonds are arranged within each molecule. The physical idea is that when one takes a step towards a bond the first segment of the bond shields the second segment and thereby prevents it from being occupied (stepped into). In the counting process one allows for this fact by subtracting out the shielded segments. One obtains

$$D_i = \frac{D V'_0}{1 - \alpha_i V'_r \left(1 - \frac{1}{r}\right)} \quad \text{III (10)}$$

This formula is valid for any lattice. In the appendix these results are recast in terms of the order parameter. In order to be able to compare the results of this section to those of the other sections we must relate  $V'_0$  to  $V_0$ . In the other two models  $V_0$  is the volume fraction of Space unoccupied by cylinders and that includes both solvent molecules and holes. In LASH  $V'_0$  is the number fraction of solvent only. If the cylinders are of length  $r$  and radius  $a$  and if each one is contained in a parallelepiped of length  $r$  and square cross-section with side  $2a$ , then the ratio of the total volume not occupied by cylinders to the total volume is

$$\frac{(4a^2 - \pi a^2)(rN_r) + 4a^2 N_0}{4a^2(rN_r) + 4a^2 N_0} \quad \text{III (11)}$$

Therefore,

$$V_0 = 0.215 + 0.785 V'_0 \quad \text{III (12)}$$

### COMPUTER MODEL (CASH)

The molecular dynamics method<sup>9</sup> enables one to calculate static and dynamic properties of model systems from a solution of Newton's equations of motion. We have applied this technique to the lyotropic liquid crystal model in order to study the diffusion of spherical particles imbedded in a liquid crystal host. The computer model consists of a cube containing spheres (the diffusing particles) and symmetrically placed cylinders (the liquid crystal). The cylinders are aligned along the  $z$ -axis of the box and extend for the entire box length. The length of the cube,  $L$ , is determined by

$$L = \left[ \frac{\pi \sigma_s^3 N_s}{6 n_s} \right]^{1/3} \quad \text{IV (1)}$$

where  $\sigma_s$  is a sphere diameter,  $N_s$  the number of spheres, and  $n_s$  the volume

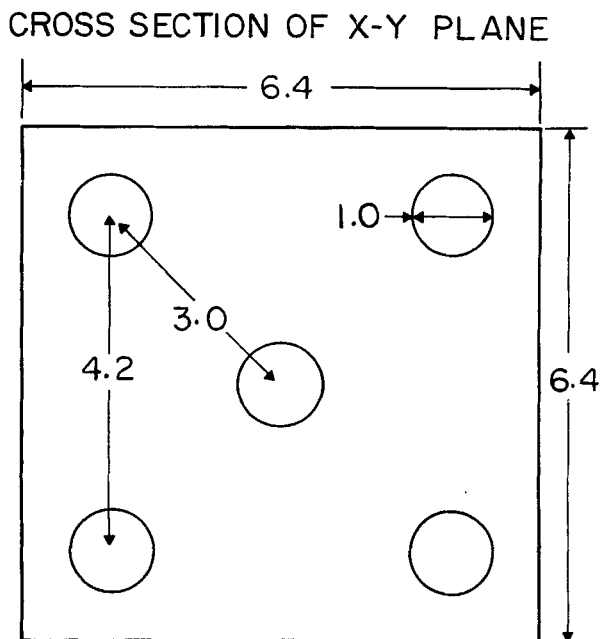


FIGURE 1 Cross-section of  $x$ - $y$  plane for the case of five symmetrically placed cylinders. Distances are in units of  $\sigma$ .

fraction of spheres. The number of spheres and cylinders which can be examined is limited by the speed and storage capacity of the computer available. The cylinders are assumed to be massive when compared to the spheres so that they are stationary on the time scale of the sphere motion. The system therefore represents a model for the motion of spherical objects through a cylindrical matrix and, hence, the machine costs are determined by the number of spheres studied. Computer time limitations confined us to systems containing one hundred spheres and various numbers of cylinders. Studies have been made with one, two, four and five cylinders which are placed symmetrically in the cube. A cross-section of the  $x$ - $y$  plane for the 5 cylinder case is shown in Figure 1. Note that the spheres are given the same diameter as the cylinders in all of these calculations.

In order to solve Newton's equations one must have the interaction potential of the model particles. The spheres interact via a Lennard-Jones 6-12 potential while the sphere-cylinder interactions follow a Lennard-Jones 5-11 potential which results when the 6-12 form is integrated over the cylinder axis:

$$U(R) = \frac{3\pi}{2} \left[ \frac{21}{32} R^{-11} - R^{-5} \right] \quad \text{IV (2a)}$$

$$R = [(R_x^s - R_x^c)^2 + (R_y^s - R_y^c)^2]^{1/2} \quad \text{IV (2b)}$$

where  $R_x^s$  is the  $x$ -component of the sphere position,  $R_x^c$  is the  $x$ -component of the cylinder position and  $R_y$  represent the  $y$ -component. This potential has a longer range than the usual 6-12 (see Figure 2) and so the cut-off was taken as 2.75 instead of 2.5. All of our calculations are done in the following reduced units: length in units of  $\sigma$ , velocity in units of  $(\epsilon/m)^{1/2}$ , and time in units of  $(1/\sigma)(\epsilon/m)^{1/2}$  where  $\sigma = 3.405\text{\AA}$ ,  $\epsilon = 119.8k_B$  and  $m = 39.95 \times 1.66 \times 10^{-24}$  gm. These are the parameters of the 6-12 potential of argon. A sphere volume fraction of 0.2 fixes the cube length as 6.397. In order to minimize surface effects and to simulate an infinite system, periodic boundary conditions are imposed on the equations of motion. A given particle in the box interacts with all the other box particles plus their images if these are within the range of the intermolecular potential. However, because the sphere potential range is less than  $L/2$  the particle can interact only with the closest image of another box particle if it doesn't interact with the box particle itself. Periodic boundary conditions have the consequence that when a particle leaves the box through one face, its image enters the opposite face, thus preserving the number of particles in the box. These boundary conditions set  $r = \infty$  in all of the formulae of Sect. III.

The solution of Newton's differential equations of motion requires a set of

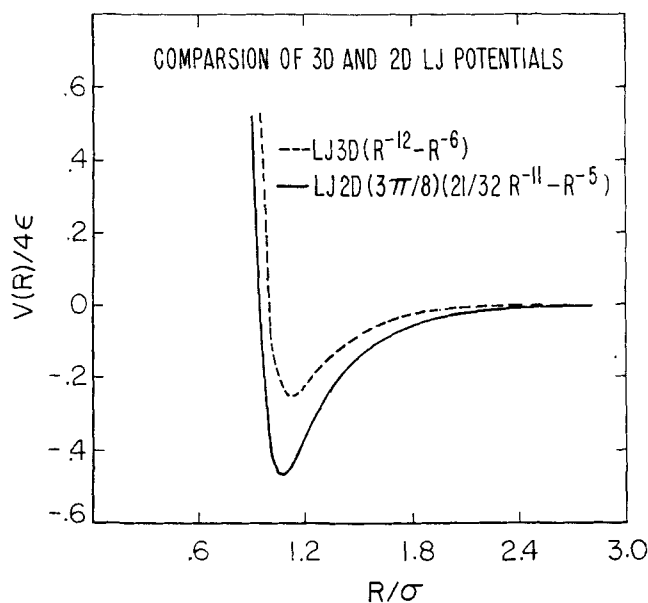


FIGURE 2 Comparison of three and two dimensional Lennard-Jones potentials. *LJ3D* represents sphere-sphere interactions; *LJ2D* represents sphere-cylinder interactions.

initial conditions and a numerical algorithm for casting the continuous differential equation into a discrete representation needed for the computer. The initial conditions are specified by starting the spheres from random positions and with velocities selected from a Maxwellian distribution. The Runge-Kutta-Gill algorithm was chosen to integrate the equations. A step of 0.01 (or  $2 \times 10^{-14}$  sec) was used in all our calculations. Since there is no *a priori* guarantee that the initial arbitrary configuration is an equilibrium one, the approach the equilibrium was monitored by following the size of the temperature fluctuations. Fifty initial steps were sufficient for equilibration. After equilibrium was reached the equations were solved for many additional steps and the positions, velocities, and accelerations were placed on 9-track magnetic tape for later analysis. Energy was conserved to 0.3% over 1000 steps.

Diffusion coefficients can be obtained in two ways from the stored data. One can either integrate the velocity autocorrelation function via a Green-Kubo relation:

$$D_{xx} = \int_0^{\infty} \langle V_x(t) V_x(0) \rangle dt \quad \text{IV (3)}$$

or find the slope of the mean-square displacement vs. time in the Einstein formula:

$$D_{xx} = \frac{1}{2t} \langle (X(t) - X(0))^2 \rangle \quad \text{IV (4)}$$

Unfortunately, the periodic boundary conditions limit the times which can be examined to those shorter than  $L/c$  where  $c$  is the sound velocity. For times longer than this a disturbance which arises in one region of the box can cross the box and enter the opposite face leading to spurious recurrences. In our systems this limiting time is  $\approx 120$  steps. Since it takes almost this long for the mean-square displacement to reach the linear region from its early  $t^2$  behavior (see Figure 3),  $D$  must be determined by the integration method. The velocity autocorrelation function was determined for each direction by the following averaging procedure:

$$\langle V(t) V(0) \rangle = \frac{1}{N_p} \frac{1}{N_0} \sum_{j=1}^{N_p} \sum_{i=1}^{N_0} V_j(t+i) V_j(i) \quad \text{IV (5)}$$

where  $N_p = 100$  (the number of particles) and  $N_0 = 400$  (the number of time origins). The normalized velocity autocorrelation functions (NVAF),  $\Psi(t)$ , are displayed in Figures 4–6. The noise builds with time so that it is difficult to extract the true function between points 50 and 120. It is seen that the NVAF components decrease more rapidly at higher cylinder densities (each additional cylinder increases the volume fraction of cylinders by 0.02). This is a reflection of the increased cross-section which hinders the sphere motion. The ratios of

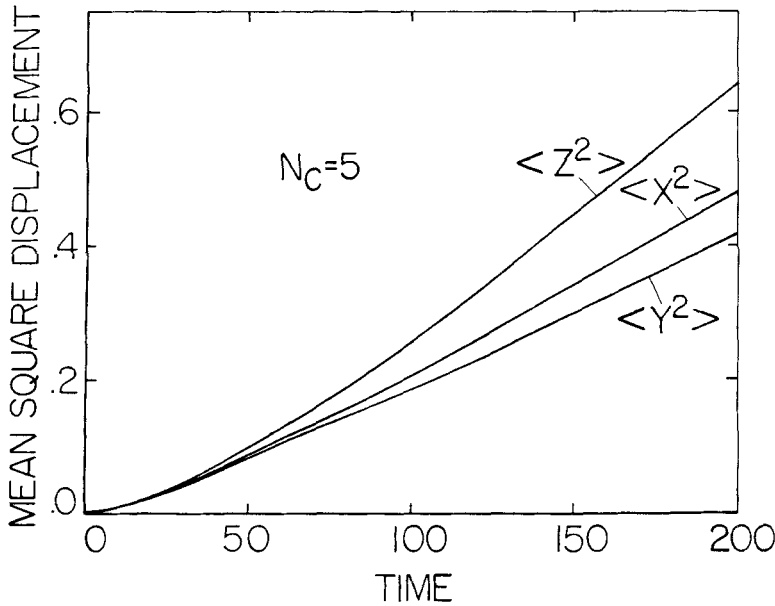


FIGURE 3 Mean-square displacement of the spheres vs time for the five cylinder case. Each time step is  $2 \times 10^{-14}$  sec.

interest,  $R = \frac{D_{\perp}}{D_{\parallel}}$  and  $R' = \frac{D_{\perp}}{D_T}$  are formed by averaging the  $D_x$  and  $D_y$  components to give  $D_{\perp}$  and  $D_x$ ,  $D_y$  and  $D_z$  to give  $D_T$ .  $D_z$  is  $D_{\parallel}$ . Note that  $R' = 3R(1 + 2R)$ .

It is of interest to examine the structure of the solution around the cylinders. We define the cylinder-sphere pair distribution function,  $g(R)$ .

$$g(R) = \frac{\langle n(R) \rangle}{n(2\pi LR \Delta R)} \quad \text{IV (6)}$$

where  $n$  is the uniform sphere number density ( $100/L^3 = 0.382$ ),  $R$  is the distance from the center of the cylinder,  $\Delta R$  the width of the cylindrical volume element ( $\Delta R = 0.01$ ),  $L$  the cylinder length, and  $\langle n(R) \rangle$  the average number of spheres in the volume element. This function was determined for the 5 cylinder case because  $\langle n(R) \rangle$  could be averaged over the cylinders to improve the statistics.  $g(R)$  is presented in Figure 7. There is a large first peak and a smaller second peak. If the spheres had condensed on the cylinder to form a solid, we would expect to find  $6 \times 6-36$  first neighbors. In the case of a random arrangement of spheres around the cylinders (e.g. a gas) one should find  $n\pi L[(3/2)^2 - 1]$  or 9.58 first neighbors. Eq. (6) can be integrated to give an expression for the number of neighbors in a given shell.

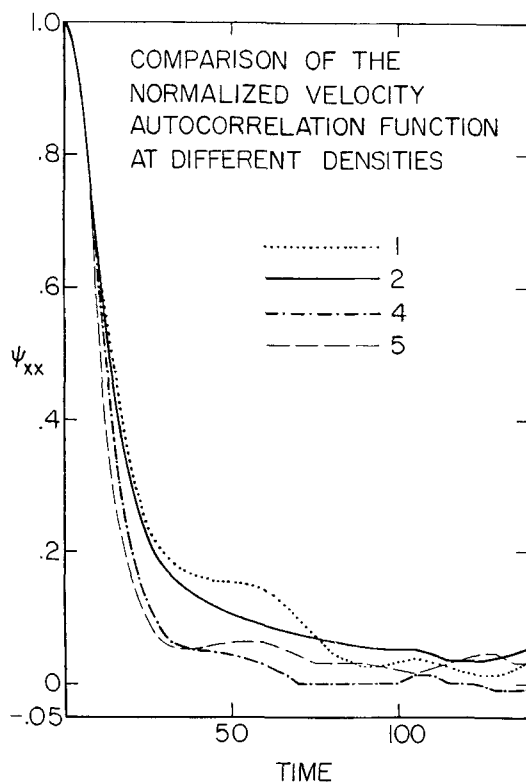


FIGURE 4 The  $xx$  component of the normalized velocity autocorrelation function for different numbers (see graph) of cylinders in the cube. Each time step is  $2 \times 10^{-14}$  sec.

$$n(R) = 2\pi L n \int_0^R G(s) s ds \quad \text{IV (7)}$$

When the integration is performed over the first peak one obtains 18.4 first neighbors. Hence, our model "looks" like a liquid. Note that the temperature of the system is .802 which is in the range of temperatures at which argon is a liquid at normal pressure.

## DISCUSSION OF RESULTS

Each of the analytical methods used here is expected to be valid in different limits of sphere size and density. DASH should apply whenever conditions are appropriate to Fickian diffusion. They are: (1), the mean free path of the diffusing molecule is short compared to the space intervals of interest. (2) The

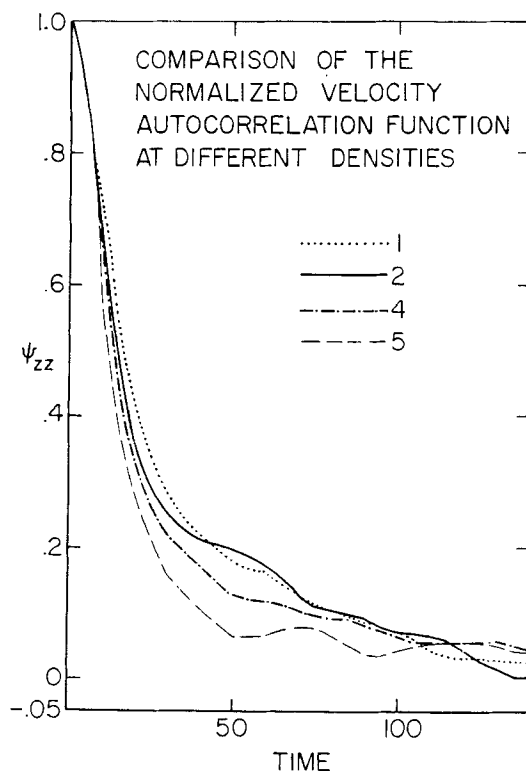


FIGURE 5 The  $yy$  component of the normalized velocity autocorrelation function for different numbers (see graph) of cylinders in the cube. Each time step is  $2 \times 10^{-14}$  sec.

mean free path is small compared to the dimensions involved in the boundary conditions. Thus, DASH should apply when the spheres are small compared to the diameters of the rods and when the density of rods is low to moderate. LASH should apply when the spheres are comparable in diameter to the diameter of the rods and when the concentration of the rods is high. This latter restriction arises because the lattice model calculations are expected to be accurate only in the high density range,<sup>10</sup> though attempts to generalize the model to lower concentrations exist.<sup>11</sup>

Figure 8 is a comparison of  $R = D_{\perp}/D_{\parallel}$  and Figure 9 is a comparison of  $R' = D_{\perp}/D_{\tau}$  as predicted by each of the models. Both the DASH and LASH expressions must break down as the cylinders begin to get close-packed.  $R$  (and  $R'$ ) will go to zero at different cylinder volume fractions (or  $1 - V_r$  for holes and solvent) depending upon the closed-packed configuration. The point 0.215 corresponds to cubic two dimensional close-packing. The curves are not extended lower than  $V_o$  equal 0.5 for the DASH model because we do not know how they



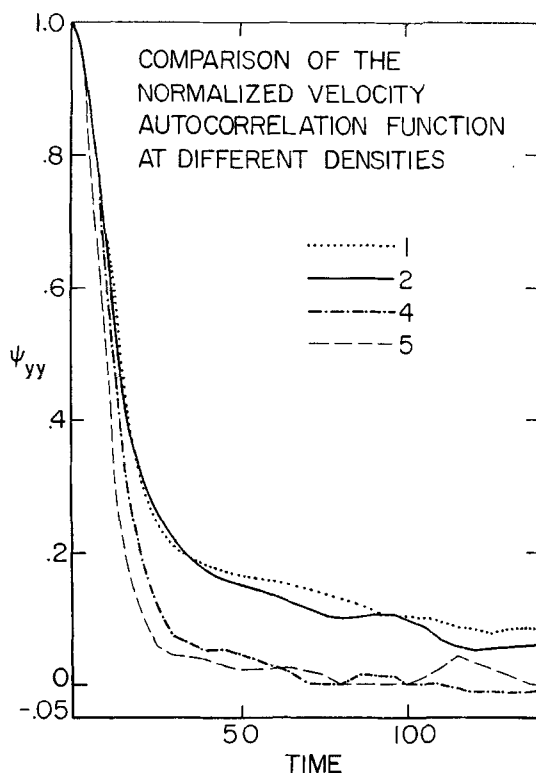


FIGURE 6 The  $zz$  component of the normalized velocity autocorrelation function for different numbers (see graph) of cylinders in the cube. Each time step is  $2 \times 10^{-14}$  sec.

come into the point 0.215. CASH results are denoted by squares and circles which refer to different time cut-offs of the upper limit in the Green-Kubo expression. While none of the analytical models agrees well with the computer data, DASH (Nielson) seems to be better than LASH at the low cylinder densities investigated ( $V_r \leq 0.1$ ). Note that the cube is quite crowded, even though the volume fraction of cylinders is low, because the corners are nearly excluded from the sphere motion. This happens because CASH requires the spheres to be inside the cube and this is progressively more difficult near the corners as the cylinders begin to occupy corner positions. In order to study higher cylinder volume fractions the programs could be rerun with the spheres having a smaller size. Even the low volume fraction results have a large scatter which could be reduced by treating larger systems of spheres for long times. We feel that additional expenditure is unjustified at this time because of the paucity of experimental data. Each of the three methods used here can be improved upon. We

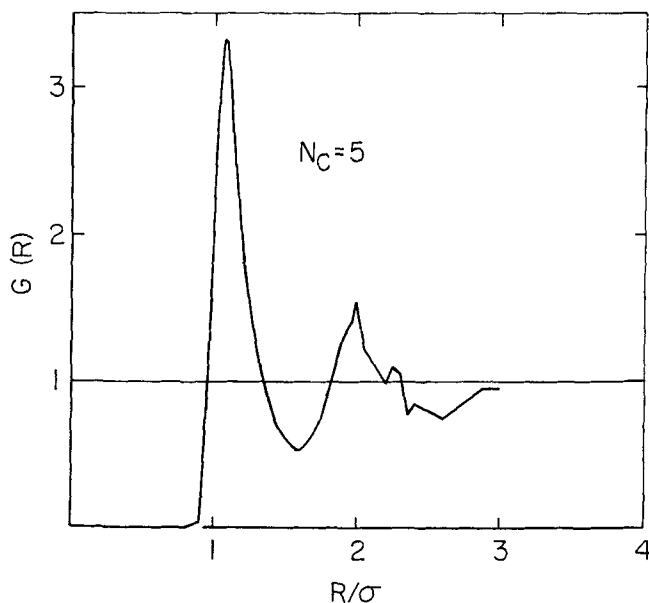


FIGURE 7 The cylinder-sphere pair correlation function for the five cylinder case.

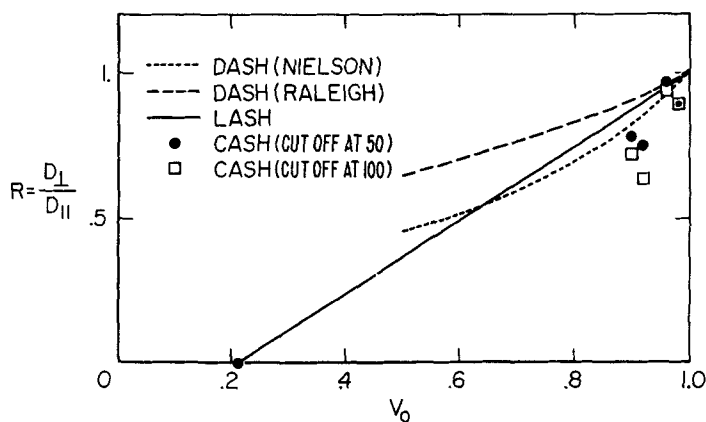


FIGURE 8 The asymmetry ratio,  $D_{\perp}/D_{\parallel}$ , for each of the models as a function of volume fraction  $V_0$ . The point 0.215 corresponds to two dimensional cubic close-packing.

wish here to indicate the direction in which such improvements would lead without however attempting the improvements themselves.

The diffusion approach lends itself to analogue computer techniques. A medium of uniform conductivity (preferably a gel) can be imbedded with non-conductive particles of the same shape as the solute molecules in the liquid

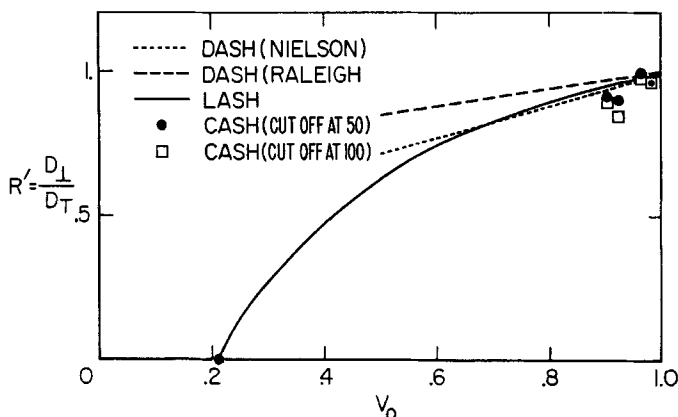


FIGURE 9 The ratio,  $D_L/D_T$ , for each of the models as a function of volume fraction  $V_0$ . The point 0.215 corresponds to two dimensional cubic close-packing.

crystal. With such a system the variation of conductivity as a function of size and shape of the particles as well as their volume fraction and orientation can be easily obtained. By preparing the system suitably one can hope to mimic the randomness which occurs in the real solvent solute system. Perhaps the easiest system on which to make measurements is the two dimensional conductive sheet. This material provides an analogue for both the two dimensional liquid crystal problem and for the case of a parallel array of long rods in three dimensions. The work of Barrer *et al.*<sup>3</sup> with conductive paper is interesting since it shows that use of random arrays give the same results as regular arrays. Analytical techniques for solving random systems are relatively undeveloped.

The lattice model approach relies on the presumption that we have correctly counted the number of ways to pack polymer molecules on a lattice (validity of Flory-Huggins<sup>12</sup> lattice method). However, there is no way to determine the errors in the Flory-Huggins lattice method since only the dimer problem has been solved exactly.<sup>13</sup> Our lattice approach would benefit from whatever improvements are made in the lattice treatments. However, our development is even more limited. First, it is assumed that the diffusing particle steps in one of three mutually perpendicular directions when in reality it can step into a continuum of angles. Second, we assumed that the length of a step was one lattice bond length long when in reality it could step greater distances. A third factor is that the particle does not really forget its past as the Markoffian assumption implies. When a particle steps into a hole it leaves a hole in the place from which it stepped from. Until this hole is filled it is more probable that the particle will step back into the hole than any other place.

The simulation of dynamics on the computer is limited by money constraints

and by the limited ability of the computer. Perhaps the most severe restriction is small sample size. The small sample size is a consequence of the money limit on the product of the number of particles and their complexity of interaction. Had we used mobile, finite length cylinders the problem would have been hopeless.

We have not yet discussed the diffusion of the rods themselves. This problem involves simultaneous translational and rotational diffusion. To our knowledge, this problem has not been solved even for an isolated, asymmetric rigid particle much less for a collection of such particles. Nevertheless we can gain some insight by discussing the translational and rotational aspects of the problem separately.

Consider a parallel array of rigid rods. Now attempt to translate one of the rods one lattice unit in the parallel direction, and one unit in the perpendicular direction. In order to translate parallel one needs only one vacant site, but to translate perpendicularly one needs  $r$  contiguous vacant sites. Accordingly the diffusion coefficients become

$$D_{\parallel} = \frac{V'_0 D_{\parallel}(0)}{1 - V'_r \left(1 - \frac{1}{r}\right)}, \quad D_{\perp} = V_0'' D_{\perp}(0) \quad \text{V (1)}$$

where we have indicated by  $D_{\parallel}(0)$  and  $D_{\perp}(0)$  the fact that diffusion of a rod in dilute solution depends on the direction of motion relative to the orientation of the rod. Thus, the translational diffusion coefficients are highly asymmetric.

The fact that  $r$  contiguous sites had to be empty in order for the molecule to translate in the  $\perp$  direction caused  $D_{\perp}$  to be exponential in  $r$ . This same feature causes the rotational diffusion coefficient to be exponential in  $r$ . A simple calculation yields

$$D_{\Omega} = V_0' \frac{r}{2} \cos \theta M_0 \frac{r}{2} \sin \theta D_{\Omega}(0) \\ M_0 = V_0' / \left(1 - V_r' \left(1 - \frac{1}{r}\right)\right) \quad \text{V (2)}$$

where  $D_{\Omega}$  is the rotational diffusion coefficient in pure solvent.

One can also calculate the effective potential in which each rigid rod is immersed due to the presence of the other rods. The probability of being at an angle  $\theta$  is according to Boltzmann's law

$$f(\theta) \propto \exp(-U(\theta)/kT) 2\pi \sin \theta \quad \text{V (3)}$$

But  $f(\theta)$  can be calculated and according to our statistics is given by

$$p = M_0^r \cos \theta V_0'^r \sin \theta \quad \text{V (4)}$$

Thus, the effective potential is given by

$$f(\theta_1)/f(\theta_2) = \exp \frac{-[U(\theta_1) - U(\theta_2)]}{kT} = \frac{M_0^r \cos \theta_1 V_0'^r \sin \theta_1}{M_0^r \cos \theta_2 V_0'^r \sin \theta_2} \quad \text{V (5)}$$

which serves to determine  $U$  (to within a constant). Having determined  $U$  and  $D_\Omega$ , the rotational diffusion characteristics can in principle be determined from the Smoluchowski<sup>14</sup> diffusional equation.

$$\frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \left( D_\Omega \frac{\partial f}{\partial \theta} + \frac{\partial U}{\partial \theta} \frac{f D_\Omega}{kT} \right) \right] \quad \text{V (6)}$$

Notice that  $D_\Omega$  is angle dependent. In view of the fact that in reality translational and rotational diffusion are coupled, it is probably sufficient to stop at the level of complexity evidenced by Eq. (6). It is interesting to notice that the Maier-Saupe theory of liquid crystals<sup>15</sup> can be generalized to include the effects of orientation caused by hard core interactions by including the term  $U(\theta)$  in the Maier-Saupe energy term.

We cannot at the present time compare our theoretical diffusion asymmetry ratios with experimental measurements on lyotropic liquid crystals because no such experiments have been reported. The few asymmetric diffusion coefficient measurements in the literature have been for thermotropic liquid crystals. Yun and Fredrickson<sup>16</sup> employed a flow diffusion experiment to determine  $R$  for nematic p-azoxyanisole (PAA). They found that  $R$  equaled 0.80 at 398° K ( $R' = 0.92$ ). Janik *et al.*<sup>17</sup> used neutron scattering to find  $R$  for PAA. They concluded that  $R$  was equal to 0.52 between 396-399° K. ( $R' = 0.77$ ). In addition they found that the self-diffusion coefficient for PAA is  $1.34 \times 10^{-5}$  cm<sup>2</sup>/s while Yun and Fredrickson obtained  $0.35 \times 10^{-5}$  cm<sup>2</sup>/sec! Indeed, there is some question about the validity of the neutron method because it is impossible to separate the contribution of rotation and translation to the diffusion coefficient in this experiment. Blinc *et al.*<sup>18</sup> have developed an NMR method which can be used to study self diffusion in liquid crystals. They do not report the magnitude of the diffusion anisotropy but do indicate that  $D_{\parallel} > D_{\perp}$  for paramethoxylbenzilidenebutylaniline (MBBA).

The experimental measurements indicate that the diffusion anisotropy is not very high. This parallels our findings with the lyotropic liquid crystals.

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It has come to our attention that Murphy and Doane (J. A. Murphy and J. W. Doane, *Mole. Cryst. and Liq. Cryst.*, **13**, 93 (1971) have measured  $D_{\perp}/D_{\parallel}$  for the diffusion of tetramethylsilane (a 'spherical' molecule) in a MBBA host by an NMR method. They report  $D_{\perp}/D_{\parallel} = .25$  for a mole fraction of TMS equal to 5%. Their result is consistent with our theoretical treatment.

## Appendix

## LATTICE MODEL CALCULATION OF THE DIFFUSION COEFFICIENT AS A FUNCTION OF ORDER PARAMETER

In conformity with conventional practice we can define an order parameter as

$$S = \frac{\langle 3 \cos^2 \theta - 1 \rangle}{2} = \frac{3}{2} \int f(\Omega) \cos^2 \theta d\Omega - \frac{1}{2} \quad (1)$$

where  $f(\Omega)$  is the distribution function for the orientation of the rigid rods. Notice that  $S=1$  for complete parallel ordering and  $S=0$  for random ordering. We seek a relation connecting  $D_{\parallel}$  and  $D_{\perp}$  to  $S$ . This relation must be approximate in nature since the proper statistics in the continuous case contains the variable

$$\mathcal{L} = 1 - \langle \sin \epsilon \rangle ; \quad \sin \epsilon = \int f(\Omega_1) \sin(\Omega_1, \Omega) d\Omega \quad (2)$$

and  $\mathcal{L}$  cannot be expressed in terms of  $S$ . The route we will take is to express  $S$  in terms of  $\alpha$ , then use Eq. III (8) to express  $D_{\perp}$ ,  $D_{\parallel}$  in terms of  $S$ . Define a quantity

$$\mathcal{L} = \frac{3\alpha_1 - 1}{2} \quad (3)$$

$\mathcal{L}$  also equals 1 for complete order and 0 for complete randomness. Let us now attempt to associate a real polymer system (with a given  $f(\Omega)$ ) with a cubic system having an  $\alpha$ , given by

$$\alpha_1 = \int f(\Omega) \cos^2 \theta_1 d\Omega \quad (4)$$

Consistency requires that

$$\alpha_2 = \int f(\Omega) \cos^2 \theta_2 d\Omega \quad (5)$$

$$\alpha_3 = \int f(\Omega) \cos^2 \theta_3 d\Omega \quad (6)$$

where  $\alpha_2$  is the fraction along the  $x$ -axis and  $\theta_2$  the angle between  $r$  and the  $x$ -axis. Because of the relation

$$\cos \theta_2 = \sin \theta_1 \cos \phi \quad (7)$$

$$\cos \theta_3 = \sin \theta_1 \sin \phi$$

we obtain

$$\alpha_1 + \alpha_2 + \alpha_3 = 1 \quad (8)$$

which shows that the assignment is consistent. One notes also that the distribution,  $f(\Omega)$  given by

$$f(\Omega) = \alpha_1 \delta(\Omega, \Omega_1) + \alpha_2 \delta(\Omega, \Omega_2) + \alpha_3 \delta(\Omega, \Omega_3) \quad (9)$$

represents a system in which  $\alpha_i$  of the molecule lies in direction  $i$ . Use of the prescription given by Eqs. (4, 5, 6) does indeed give such a lattice. We therefore use Eqs. (4, 5, 6) (and the relation  $\mathcal{L} = S$ ) to associate a cubic lattice model ( $\alpha_1, \alpha_2, \alpha_3$ ) with a continuous model  $f(\Omega)$ . We assume that calculations on the lattice model will be accurate for the associated continuum model.

One obtains immediately from Eq. III (9) and Eq. (4)

$$D_{\parallel} = \frac{D V'_0}{1 - \frac{(2S+1)}{3} V'_r (1 - \frac{1}{r})}, \quad D_{\perp} = \frac{D V'_0}{1 - (\frac{1-S}{3}) V'_r (1 - \frac{1}{r})} \quad (10)$$

For an  $f(\Omega)$  that is not cylindrically symmetric one can define three order parameters

$$S_i = \frac{\langle 3 \cos^2 \theta_i - 1 \rangle}{2} = \frac{3}{2} \alpha_i - \frac{1}{2} \quad (11)$$

and III (10) becomes

$$D_i = \frac{D V'_0}{1 - \frac{(2S_i+1)}{3} V'_r (1 - \frac{1}{r})} \quad (12)$$

In our model  $S$  equals one so that Eq. III (8) is recovered from Eq. (10).

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### References

1. Chistyakov, I.G., *Sov. Phys. Uspekhi* **9**, 551 (1967), Brown G.H., Doane, J.W. and Neff, V.D., *Critical Reviews in Solid State Sciences*, Sept., 305 (1970).
2. Private communication.
3. Barrer, R.M., Barrie, J.A., and Rogers, M.G., *J. Polymer Science A*, **1** 2565 (1963).
4. Synge, J.L. and Schild, A., *Tensor Calculus* (University of Toronto Press, Toronto, 1949), p. 20.
5. Hill, H.T., Puro, W.O. and Bowie, D.M., *Proc. IRE*, **44**, 171 (1956), Ashton, J.F., Halpin, J.C. and Petit, P.H., *Primer on Composite Materials Analysis* (Technomic, Stamford, Conn., 1969), Chap. 5. Nielson, L.E., "The electrical and thermal conductivity of two phase systems," report from Monsanto/Washington University #HPC 72-153 (1972).
6. Rayleigh, L., *Phil. Mag.* **34**, 481 (1892).
7. DiMarzio, E.A., *J. Chem. Phys.* **35** 658 (1961).
8. DiMarzio, E.A., *J. Chem. Phys.* **36**, 1563 (1962).
9. Berne, B.J. and Forster, D., *Ann. Rev. Phys. Chem.* **22**, 563 (1971).

10. Flory, P.J., *Principles of Polymer Chemistry*, (Cornell University Press, Ithaca, New York, 1953), pp. 495-505.
11. Yamamoto, M. and White, J.L., *Macromolecules* **5**, 58 (1972) and references therein.
12. Flory, P.J., *J. Chem. Phys.* **10**, 51 (1942). Huggins, M.L., *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).
13. Fisher, M.E., *Phys. Rev.* **124**, 1664 (1961). Temperley, H.N.V. and Fisher, M.E., *Phil. Mag.* **6**, 1061 (1961). Kasteleyn, P.W., *Physica*, **27**, 1209 (1961).
14. Chandrasekhar, S., *Rev. Mod. Phys.* **15**, 1 (1943).
15. Maier, W. and Saupe, A., *Z. Naturforsch* **14A**, 882 (1959). Maier, W. and Saupe, A., *Z. Naturforsch* **15A**, 287 (1960).
16. Yun, C.K. and Fredrickson, A.G., *Mol. Cryst. Liq. Cryst.* **12**, 73 (1970).
17. Janik, J.A., Janik, J.M., Otnes, K. and Pynn, R., *Neutron Inelastic Scattering* (International Atomic Energy, Vienna, 1972), p. 515.
18. Blinc, R., Dimic, V., Pris, J., Vilfon, M. and Zupancic, I., *Mol. Cryst. Liq. Cryst.* **14**, 97 (1971). Blinc, R., Pris, J., and Zupancic, I., *Phys. Rev. Letters* **30**, 546 (1973). Blinc (private communication) has indicated a value of approximately 1.3 for  $D_{\parallel}/D_{\perp}$ .