

Monte Carlo simulations of solute ordering in nematic liquid crystals: Shape anisotropy and quadrupole-quadrupole interactions as orienting mechanisms

James M. Polson*

Department of Physics, University of British Columbia, 6224 Agricultural Road, Vancouver, British Columbia, Canada V6T 1Z1

E. Elliott Burnell†

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

(Received 16 August 1996; revised manuscript received 2 December 1996)

Monte Carlo computer simulations were used to investigate the effects of shape anisotropy and electrostatic interactions as mechanisms for orientational ordering of solutes in nematic liquid crystals. The simulation results were analyzed in terms of two theories of solute ordering which derive mean-field orientational potentials from the intermolecular pair potential. In the calculations, solute and solvent molecular shapes were approximated by hard ellipsoids. Most simulations also incorporated the interaction between point quadrupole moments placed at the centers of the ellipsoids. In the hard-core systems, orientational order parameters and distribution functions were calculated for a collection of different solutes under a variety of conditions. A theory due to Terzis and Photinos [Mol. Phys. **83**, 847 (1994)] was found to underestimate the effect of shape anisotropy on orientational ordering drastically. The introduction of an effective solvent packing fraction was unable to improve the predictive power of the theory significantly. The quadrupolar systems were used to investigate a mean-field model for solute ordering which considers an interaction between the solute molecular quadrupole moment with an average electric-field gradient. The simulations indicate that the electric-field gradient sampled by the solute is highly dependent on the properties of the solute, contrary to some experimental evidence. Further, the effects of the intermolecular quadrupolar interactions on orientational ordering and the electric-field gradient were analyzed using a mean-field potential derived here and based on the theory due to Emsley, Palke, and Shilstone [Liq. Cryst. **9**, 649 (1991)]. This model was found to provide a qualitatively correct but quantitatively imprecise prediction of orientational ordering. [S1063-651X(97)14003-X]

PACS number(s): 61.30.Cz, 61.20.Ja

I. INTRODUCTION

The property of orientational ordering in the nematic liquid-crystalline phase arises from the presence of anisotropic intermolecular forces. Important examples of these include short-range repulsive forces and long-range dispersion, electrostatic and induction interactions. Among these, the short-range interaction, coupled with the high degree of shape anisotropy typical for most nematogens, is generally believed to be the principal factor underlying the stability of the phase [1–4]. The long-range interactions, which arise from the presence of permanent molecular electrostatic multipole moments and polarizabilities, are believed to have a smaller effect on the molecular ordering. An important objective in the study of liquid crystals is the attempt to gain a detailed understanding of the effects of each of the components of the intermolecular pair potential on the structure of the phase. While this understanding is not yet complete, significant progress has been achieved through a combination of experimental, theoretical and, more recently, computer simulation techniques.

Nuclear magnetic resonance (NMR) has long been recognized as an excellent experimental technique for studying

orientational ordering in liquid crystals [5–7]. An analysis of the spectra of orientationally ordered molecules provides values of various NMR coupling constants, which in turn yield second-rank orientational order parameters. However, application of the technique to study the nematogens themselves can be complicated by the structural complexity and inherent flexibility of the molecules. These factors tend to complicate the analysis of both the spectra and the NMR coupling constants, and thus to preclude an accurate measurement of orientational order. This problem can be circumvented by the use of probe solutes, which in principle sample the same intermolecular forces that order the nematogens. Generally, a rigid molecule with lower than T_d symmetry will be partially oriented when dissolved in an anisotropic nematic environment. Solute may be chosen to simplify the spectral analysis and interpretation of the coupling constants; rigid solutes with relatively few nuclear spins are ideal. In addition, specific solutes may be chosen to highlight the effects of a specific intermolecular interaction on orientational ordering. By contrast, when studying the behavior of the nematogens alone, it is difficult to gauge the relative importance and effects of the various intermolecular forces. Below, we briefly review some of the important studies employing probe solutes to study intermolecular forces in nematic liquid crystals.

Direct evidence of a specific intermolecular interaction as an orientational ordering mechanism was obtained in several studies employing deuterated molecular hydrogen as a solute in a nematic liquid crystal [8,9]. In particular, it was found

*Present address: FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands. Electronic address: polson@amolf.nl

†Electronic address: bur@chem.ubc.ca

that the interaction of the molecular quadrupole moment of both D_2 and HD with an average electric-field gradient (EFG), which was measured directly from the analysis of the 2H NMR spectrum, provided a very accurate prediction of orientational ordering for these particular solutes [10]. It is not unreasonable to hypothesize that all probe solutes experience a similar interaction between their quadrupole moments and an average EFG. However, to apply this result to the analysis of order parameters of other solutes, it is necessary to assume that the EFG is a property of the nematic solvent alone, and not influenced significantly by solute properties. This approximation is required because the EFG can only be measured directly for the deuterated hydrogens, where the internal EFG contribution to the NMR quadrupolar coupling constant can be calculated accurately. Unfortunately, it is difficult to test this hypothesis directly due to the presence of additional ordering mechanisms, most notably anisotropic short-range repulsive forces, which are non-negligible for larger molecules. Consequently, predictions of order parameters for a variety of solutes using known values of quadrupole moments and values of the EFG measured with molecular hydrogen tend to be poor [11,12]. However, some experimental evidence of the validity of this model has been observed in the orientational behavior of specific solutes. For example, acetylene, like D_2 , orients with a negative order parameter in the nematic solvent *N*-4-ethoxybenzylidene-4'-*n*-butylaniline (EBBA) [12–14], a solvent which was determined to have a negative EFG. While it is difficult to rationalize this behavior by invoking the presence of other orienting mechanisms, it is the predicted result for a molecule with a positive quadrupole moment which interacts with a negative EFG. Similarly, the behavior of the order parameters for benzene and hexafluorobenzene, molecules with very similar shapes, but with quadrupole moments of opposite signs, follows the pattern predicted by the quadrupole-moment–EFG mechanism using values of the EFG obtained from D_2 for various nematic solvents [12]. Finally, the presence of nonvanishing dipolar and quadrupolar coupling constants for deuterated methanes in a nematic solvent can be understood as arising from a vibration-rotation coupling that results from a second-rank tensorial interaction between the solute and a solvent mean field [15]. A study of the quadrupolar coupling constants gives consistent results for theoretically solvent-independent quantities in different solvents only when an external EFG with values determined in the studies of D_2 and HD was incorporated into the analysis [16].

Emsley and co-workers have discussed the significance of the EFG and its effects on the ordering of solutes in nematic solvents using a theory for orientational ordering which is closely related to the Maier-Saupe theory of nematics [17–19]. In the context of this theory, it was shown that the nematogen quadrupole moment is the lowest order electrostatic multipole moment that provides a nonvanishing contribution to the EFG. Further, it is possible to derive an expression for both the EFG and the contribution to a potential of mean torque arising from the presence of the EFG. However, the expressions for these quantities are complicated by their dependence on the orientational distribution of solute-solvent intermolecular displacement vectors, a property which is not readily determinable by experimental methods. Thus the

theory and its assumptions are difficult to test directly by an analysis of available experimental data. Nevertheless, a study of the solvent dependence of the orientational behavior of anthracene and anthraquinone, molecules with similar shapes and polarizabilities but significantly different quadrupole moments, was undertaken and analyzed using this theory [19]. It was concluded that the distribution of solvent-solute intermolecular displacement vectors, and consequently the EFG, was strongly dependent on both solvent and solute molecular properties, in contrast to the conclusions of Burnell and co-workers.

The description of the contribution to orientational ordering from electrostatic interactions by means of a solute-independent average EFG has also been criticized by Photinos and co-workers [20–22]. They provided experimental evidence that the interaction between local dipole moments on solute and solvent molecules, in conjunction with short-range repulsive forces, provide an additional ordering mechanism [20,21]. In the context of the picture of an electrostatic mean-field introduced by Burnell and co-workers and developed theoretically by Emsley and co-workers, solute dipole moments interact with an average electric field, which is necessarily zero for an apolar nematic phase; thus the contribution to the mean-field potential should vanish. Further, Terzis and Photinos constructed a theory to account for the contributions from both short-range repulsive forces and arbitrary electrostatic interactions [22]. An interesting result of this study was that electrostatic interactions were found to provide a contribution to orientational ordering which was roughly equal to that from the anisotropic repulsive forces. In addition, it was shown that the electrostatic mean-field model of a solute molecular quadrupole moment interacting with a solute-independent mean EFG was inconsistent with their theoretical calculations.

The studies of Emsley and co-workers and Photinos and co-workers represent the only attempts to date to provide a rigorously theoretical understanding of the orientational behavior of molecules in nematic liquid crystals. The goal of these theories is to derive a mean-field orientational potential which incorporates the molecular properties, such as shape anisotropy and electric multipole moments, that give rise to the intermolecular interactions responsible for the alignment of molecules. An alternative approach is the use of empirical mean-field orientational potentials. In a series of several papers, Burnell and co-workers [23–28] studied the effects of anisotropic short-range repulsive interactions by measuring orientational order parameters for a wide collection of solutes in a nematic solvent mixture characterized by a zero EFG for D_2 and HD. It was shown that the ordering of the solutes generally were very well predicted by various model potentials that incorporate the details of the molecular size and shape anisotropy. Further, it was found that the more accurate models accounted for the molecular shape in the most detailed manner. In addition, the models could be used as an effective tool in the analysis of the conformational equilibrium of partially oriented flexible molecules [29–32]. From these studies, it was concluded that the presence of short-range repulsive interactions, which are expected to be strongly dependent on molecular shape, was the principal factor responsible for solute orientational ordering. More recently, a computer simulation study [33], undertaken to

complement this experimental work, confirmed the connection between these model potentials and the short-range forces, and provided further evidence that these forces dominate the orientational behavior of molecules in nematic solvents.

The empirical potentials used to model short-range repulsive forces in the studies described above differ considerably from the theoretical potentials of the kind presented by Terzis and Photinos, and Emsley and co-workers, in that the latter are derived from some chosen form of the intermolecular pair potential. In the derivation of these rigorous theoretical models there are two types of approximations employed whose validity determines the accuracy of the theory: (1) the modeling of the molecules and the pair potential, and (2) the mathematical approximations required to integrate over the pair potential to obtain the mean-field potential. Unfortunately, it is difficult to test the theory and the validity of the approximations using the experimental data alone. This problem is due to the fact that there are multiple contributions to orientational ordering. Experiment provides at most only a few orientational order parameters per solute, and no estimate of the relative magnitude and effect of each contribution.

Computer simulations of solutes in nematic solvents can provide an effective bridge between experiment and theory. The molecular models employed in the various theories can easily be incorporated into the simulations. A comparison of the simulation results with theory and experiment can then provide valuable insight into the validity of the models for the pair potential and the mathematical approximations used in the theory. In addition, this approach provides a simple method for examining the importance of each component of the intermolecular pair potential as an orienting mechanism, and how the complex interplay between the different contributions varies with the properties of the solute.

In this paper, we employ the Monte Carlo computer simulation method to study the combined effects of shape anisotropy and electrostatic interactions on orientational ordering of solutes in a nematic phase. In addition, we use the simulation results to test the accuracy of the theories of Terzis and Photinos, and Emsley and co-workers for solute orientational ordering in nematic solvents. We employ a minimal model for the intermolecular pair potential in order not to obscure the interpretation of the results. Specifically, we model both the solvent and solute molecules as cylindrically symmetric hard ellipsoids with point quadrupoles placed at their centers. The hard-core component of this potential is designed to approximate the repulsive forces at short intermolecular distances. Note that a variety of computer simulation studies over the past decade have demonstrated that systems of hard convex bodies such as ellipsoids can form a stable orientationally ordered nematic phase at sufficiently high densities [34–37]. The additional electrostatic interactions used here are expected to have an additional perturbative effect on the structure of the solvent. The simplified modeling of the solute molecular shape is designed to provide a computationally convenient method for investigating the effects of solute shape anisotropy on orientational ordering. We emphasize that this study is concerned with determining the general effects of molecular properties on ordering without attempting to simulate the precise behavior of any particular real

solute. Thus we study a collection of ellipsoidal solutes with a variety of sizes and dimension ratios.

The use of point quadrupoles to describe the electrostatic properties of the solvent and solute molecules is likely a far more drastic approximation. At short intermolecular distances, the quadrupole-quadrupole interaction may yield an unrealistic estimate of the electrostatic interactions between molecular charge distributions. This limitation may be particularly problematic at the high densities typical of a condensed phase. Nevertheless, there are important reasons why this model deserves to be investigated. It is important to determine the simplest model which can reproduce the main qualitative behavior observed experimentally in real nematic systems. Further, the molecular models used in the theories of orientational ordering described above also employ point electrostatic multipole moments. Thus the simulations can provide a test of the mathematical approximations employed in the derivation of the theoretical mean-field potentials. We focus on the effects of quadrupole moments alone, since a principal goal of this study is to investigate the interaction of the solute quadrupole moment with the EFG generated by the solvent, and because the quadrupole moment is the lowest order electrostatic multipole moment that the Emsley-Luckhurst theory predicts to contribute to a nonvanishing EFG. There are also important practical considerations for choosing this model. More realistic descriptions of the molecular charge distributions, such as the distribution of several point multipole moments within the volume of the molecule, would involve considerably more computational effort to calculate the pair potential in the Monte Carlo (MC) simulations. Also, quadrupole-quadrupole interactions decay as r^{-5} , which is sufficiently rapid to neglect very long-range contributions to the total energy. This also has a major influence on determining the speed with which the calculations can be performed. Dipole-dipole interactions, by comparison, decay as r^{-3} , and require the inclusion of much longer-range contributions to the total energy, as well as the use of Ewald sums to induce the convergence of the total energy with increasing system size [38]. The result is a much more time-consuming calculation.

To summarize, the description of a solvent or solute molecule as a hard ellipsoid with a point quadrupole represents a simple model with the following attributes: (1) it is computationally convenient; (2) it can be used to test the mathematical approximations in current theories of solute ordering; (3) it is a starting point to determine the basic molecular properties required to explain the orientational behavior of solutes in nematics; and (4) it can be used to investigate the individual effects of the contributions to orientational ordering from shape anisotropy and electrostatic interactions, information which is not readily obtained by experiment.

In Sec. II, we outline the basic ideas of the theoretical models developed by Terzis and Photinos [22] and Emsley and co-workers [17,18,39]. Section III describes the technical details of the Monte Carlo simulations. In Sec. IV we present the results of the simulations and discuss their significance in terms of both theoretical predictions and previous experimental results. Section V summarizes the key results of this study.

II. THEORY

A. Terzis-Photinos (TP) theory

Terzis and Photinos have developed a theory for the description of orientational order of solutes in a nematic solvent which can incorporate dispersion, induction, short-range repulsive, and electrostatic interactions between the solute and solvent molecules [22]. We repeat the brief derivation of the mean-field orientational potential presented in the original paper in order to highlight the approximations discussed later on. Note that we include the effects of the short-range and electrostatic interactions only, since the effects of induction and dispersion forces were found to be negligible.

The theoretical approach involves the reduction of the singlet distribution function of the solute, which is given by the following exact expression:

$$P(X) = Z^{-1} \int dX_1 dX_2 \cdots dX_N \tilde{P}_N(X_1, X_2, \dots, X_N) \times \exp\left[-\sum_{i=1}^N u(X, X_i)/k_B T\right], \quad (1)$$

where $X \equiv (\vec{r}, \omega)$, $\tilde{P}_N(X_1, X_2, \dots, X_N)$ is the N -particle solvent distribution function in the absence of the solute, $u(X, X_i)$ is the pair potential between the solute and the i th solvent molecule, and Z is a normalizing factor. The principal approximation of the theory is to neglect the correlations between solvent molecules,

$$\tilde{P}_N(X_1, X_2, \dots, X_N) \approx \tilde{P}(X_1) \tilde{P}(X_2) \cdots \tilde{P}(X_N), \quad (2)$$

which simplifies the expression of the solute distribution function to the following:

$$P(X) \sim \left[\int dX' \tilde{P}(X') \exp(-u(X, X')/k_B T) \right]^N. \quad (3)$$

Short-range repulsive forces are approximated by a hard-core (HC) interaction between molecules, which can take the values of zero or infinity depending on whether the molecules overlap. Anisotropic long-range interactions are restricted in this treatment to electrostatic (ES) forces. Thus the pair potential can be written as

$$u(X, X_i) = u_{\text{HC}}(X, X_i) + u_{\text{ES}}(X, X_i). \quad (4)$$

Further, for spatially homogeneous systems, $P(X) = f(\omega)/V$ and $\tilde{P}(X) = \tilde{f}(\omega)/V$. Thus the solute orientational distribution function can be written as the following:

$$f(\omega) \sim \left[V^{-1} \int d\omega' d\vec{r} \tilde{f}(\omega') \{1 - K(\vec{r}, \omega, \omega')\} \right]^N \equiv [1 - \langle K \rangle]^N, \quad (5)$$

where

$$K(\vec{r}, \omega, \omega') = 1 - g_{\text{HC}} \exp(-u_{\text{ES}}/k_B T), \quad (6)$$

and where

$$g_{\text{HC}} = \exp(-u_{\text{HC}}/k_B T). \quad (7)$$

Note that $K=1$ for overlapping particles and decays to zero with increasing r , though it has appreciable values for a small localized volume v_a , where $v_a^{1/3}$ is of the order of a few molecular diameters. The solute distribution function may be written

$$f(\omega) \sim \exp(N \ln(1 - \langle K \rangle)). \quad (8)$$

Expanding the logarithm and neglecting terms of order $(v_a/V)^2$ and higher, it is trivial to show that

$$f(\omega) \sim \exp[-N \langle K(\omega) \rangle]. \quad (9)$$

This corresponds to the following terms for the mean-field potential:

$$U(\omega) = U_{\text{HC}}(\omega) + U_{\text{ES}}(\omega), \quad (10)$$

where

$$U_{\text{HC}}(\omega)/k_B T = \rho \int d\vec{r} d\omega' \tilde{f}(\omega') [1 - g_{\text{HC}}(\vec{r}, \omega, \omega')] \quad (11)$$

and

$$U_{\text{ES}}(\omega)/k_B T = \rho \int d\vec{r} d\omega' \tilde{f}(\omega') \times [1 - \exp(-u_{\text{ES}}(\vec{r}, \omega, \omega')/k_B T)] \times g_{\text{HC}}(\vec{r}, \omega, \omega'). \quad (12)$$

As a final remark on the mean-field potential, we note that the contribution from the hard-core component of the pair potential can be written as

$$U_{\text{HC}}(\omega)/k_B T = \rho \int d\omega' V_{\text{ex}}(\omega, \omega') \tilde{f}(\omega'), \quad (13)$$

where $V_{\text{ex}}(\omega, \omega')$ is the orientation-dependent solute-solvent excluded volume. This is the same form of the potential that appears in the self-consistent expression for the orientational distribution function in the Onsager theory of the nematic-isotropic phase transition for a system of long hard rods [40]. This is not surprising, since both theories consider the effects of interactions of pairs of molecules while neglecting correlations due to three and more particles. Onsager's theory is valid in the limit of very long rods, where the effects of these higher order correlations are negligible. While the typical nematogen and solute molecules do not satisfy this condition, Terzis and Photinos argued that neglecting solvent-solvent interactions should have minor effects if the system is sufficiently far removed from the phase transition. This assumption can be tested by comparing the results of computer simulations and the theoretical predictions for solutes in nematic systems.

B. Emsley-Luckhurst (EL) theory

A theoretical model for describing the orientational ordering of solutes in a uniaxial nematic solvent has been developed by Emsley, Hashim and Luckhurst [39]. The approach of this theory is closely related to that used in the Maier-

Sauepe theory of nematic liquid crystals. A mean-field orientational potential is derived using some simplified model for the pair potential between solvent and solute molecules, and averaging over the magnitude and direction of the intermolecular displacement, and over the orientation of the solvent molecules. The relationship between the mean-field and pair potentials is given by

$$U(\omega_1) = \rho \int d\vec{r} d\omega_2 u(\vec{r}, \omega_1, \omega_2) \tilde{f}(\omega_2) g(\vec{r}), \quad (14)$$

where $\omega_1 \equiv (\theta_1, \phi_1)$ and $\omega_2 \equiv (\theta_2, \phi_2)$ are the polar angles describing the orientation of the nematic director in the solute and solvent molecular frames, respectively. Also, \vec{r} is the intermolecular displacement, ρ is the number density of the solvent, $u(\vec{r}, \omega_1, \omega_2)$ is the solvent-solute pair potential, $\tilde{f}(\omega_2)$ is the solvent orientational distribution function, and $g(\vec{r})$ is the pair correlation function. The crucial approximation of this theory involves neglecting the orientational correlations between molecules, i.e., $g(\vec{r}, \omega_1, \omega_2) \approx g(\vec{r})$.

Most applications of the Emsley-Luckhurst theory to the analysis of experimental data have employed long-range anisotropic dispersion forces, though the incorporation of an electrostatic interaction between quadrupoles to the pair potential has been discussed [17,18]. Below, we derive the mean-field potential between quadrupoles for the case of axially symmetric molecules.

The energy of two interacting axially symmetric quadrupole moments may be written as [41]

$$\begin{aligned} u_{QQ}(\vec{r}, \omega_1, \omega_2) &= (4\pi)^{3/2} \sqrt{\frac{14}{45}} \left(\frac{Q_{2,0}^{(u)} Q_{2,0}^{(v)}}{4\pi\epsilon_0 r^5} \right) \\ &\times \sum_{m_1, m_2, m} C(224; m_1, m_2, m) \\ &\times Y_{2, m_1}(\omega_1) Y_{2, m_2}(\omega_2) Y_{2, m}^*(\omega), \end{aligned} \quad (15)$$

where $C(224; m_1, m_2, m)$ are Clebsch-Gordon coefficients, $\omega \equiv (\theta, \phi)$ describe the orientation of the intermolecular vector in the frame of the nematic director, and $Q_{2,0}^{(\alpha)} = \sqrt{5/4\pi} Q_{zz}^{(\alpha)}$, where $Q_{zz}^{(\alpha)}$ is the principal cartesian component of the quadrupole moment tensor for the solute ($\alpha = u$) and solvent ($\alpha = v$). Substitution of Eq. (15) into Eq. (14) yields

$$\begin{aligned} U(\theta) &= \frac{\sqrt{280\pi}}{3} \rho \left(\frac{Q_{zz}^{(u)} Q_{zz}^{(v)}}{4\pi\epsilon_0} \right) \sum_{m_1, m_2, m} C(224; m_1, m_2, m) \\ &\times Y_{2, m_1}(\omega_1) \langle Y_{2, m_2} \rangle \left\langle \frac{Y_{4, m}^*}{r^5} \right\rangle, \end{aligned} \quad (16)$$

where

$$\langle Y_{2, m_2} \rangle = \int d\omega_2 \tilde{f}(\omega_2) Y_{2, m_2}(\omega_2), \quad (17)$$

and where

$$\left\langle \frac{Y_{4, m}^*}{r^5} \right\rangle = \int \frac{Y_{4, m}^*(\omega)}{r^5} g(\vec{r}) r^2 dr d\omega. \quad (18)$$

In the case of axial symmetry considered here, Eq. (17) reduces to

$$\langle Y_{2, m_2} \rangle = \left(\frac{5}{4\pi} \right)^{1/2} \bar{P}_2^{(\text{nem})} \delta_{m_2, 0}, \quad (19)$$

where $\bar{P}_2^{(\text{nem})}$ is the second-rank nematic order parameter, while Eq. (18) reduces to

$$\left\langle \frac{Y_{4, m}^*}{r^5} \right\rangle = 6\sqrt{\pi} \delta_{m, 0} \int \frac{\bar{P}_4^+(r) g(r)}{r^3} dr, \quad (20)$$

where $\bar{P}_4^+(r)$ is a fourth-rank order parameter describing the orientation of the solvent-solute intermolecular displacement at a distance r . Finally, substitution of Eqs. (19) and (20) into Eq. (16) yields

$$\begin{aligned} U(\theta) &= 60\pi\rho \left(\frac{Q_{zz}^{(u)} Q_{zz}^{(v)}}{4\pi\epsilon_0} \right) \bar{P}_2^{(\text{nem})} \int \frac{\bar{P}_4^+(r) g(r)}{r^3} dr \\ &\times P_2(\cos\theta). \end{aligned} \quad (21)$$

Noting that the form of the interaction between a quadrupole moment and an EFG is given by

$$U(\theta) = -\frac{1}{2} F_{ZZ} Q_{zz} P_2(\cos\theta), \quad (22)$$

Eq. (21) can be used to define an average EFG:

$$\bar{F}_{ZZ} = -120\pi\rho Q_{zz}^{(v)} \bar{P}_2^{(\text{nem})} \int \frac{\bar{P}_4^+(r) g(r)}{r^3} dr. \quad (23)$$

It is convenient to rewrite the expressions for the mean-field potential and the average EFG in terms of dimensionless quantities. We define a reduced mean-field potential $U^*(\theta) \equiv U(\theta)/k_B T$:

$$\begin{aligned} U^*(\theta) &= 60\pi Q_u^* Q_v^* \rho^* \left(\frac{d^3}{v_0} \right) \int \frac{\bar{P}_4^+(r^*) g(r^*)}{(r^*)^3} dr^* \\ &\times P_2(\cos\theta), \end{aligned} \quad (24)$$

where $Q_\alpha^* = Q_{zz}^{(\alpha)}/\sqrt{4\pi\epsilon_0 k_B T d^5}$, $\rho^* = \rho v_0$, $r^* = r/d$, v_0 is the solvent ellipsoid volume, and where d , the diameter of the solvent ellipsoid, is used to fix the length scale in the system. Further, we define a dimensionless EFG:

$$\begin{aligned} \bar{F}_{ZZ}^* &\equiv \frac{F_{ZZ} d^5}{|Q_{zz}^{(v)}|} = -120\pi\rho^* \left(\frac{d^3}{v_0} \right) \left(\frac{Q_{zz}^{(v)}}{|Q_{zz}^{(v)}|} \right) \\ &\times \bar{P}_2^{(\text{nem})} \int \frac{\bar{P}_4^+(r^*) g(r^*)}{(r^*)^3} dr^*. \end{aligned} \quad (25)$$

Finally, comparing Eqs. (24) and (25), we can write

$$U^*(\theta) = -\frac{1}{2} \bar{F}_{ZZ}^* |Q_v^*| Q_u^* P_2(\cos\theta). \quad (26)$$

In the context of the theory presented above, an essential requirement for the observation of a nonvanishing average EFG is a nonspherical distribution of solute-solvent intermolecular vectors. If this distribution had spherical symmetry, then the factor defined in Eq. (18) would vanish for all val-

ues of m , along with the magnitude of the EFG. This point was first noted by Emsley, Palke, and Shilstone who incorporated this factor into the derivation of the contribution to the mean-field orientational potential from quadrupole-quadrupole interactions [18]. However, this derivation had implicitly assumed the separability of averaging the pair potential over the magnitude and direction of the intermolecular vector \vec{r} :

$$\left\langle \frac{Y_{4,m}^*}{r^5} \right\rangle \approx \langle Y_{4,m}^* \rangle \langle r^{-5} \rangle \sim \bar{P}_4^+ \delta_{m,0} \langle r^{-5} \rangle. \quad (27)$$

However, the computer simulations of Emerson, Hashim, and Luckhurst [42] indicate that the fourth-rank order parameter \bar{P}_4^+ , which describes the nonsphericity of the intermolecular-vector distribution, is strongly dependent on the molecular separation r , and therefore that the separability of the averaging in Eq. (27) is invalid. The mean-field potential derived above for the quadrupole-quadrupole pair potential differs from that derived originally by Emsley, Palke, and Shilstone by the use of Eq. (20) rather than Eq. (27) for averaging over the intermolecular coordinates.

III. MC SIMULATIONS

The methods employed in the simulation of solutes in a nematic solvent are standard. The calculations were performed at constant volume for a fixed number of particles confined to a rectangular box subject to the usual periodic boundary conditions. The calculations used a system of 239 solvent particles plus one solute particle. Nematogens were modeled as cylindrically symmetric hard ellipsoids with an axis ratio of 5:1. Solute particles were also modeled as cylindrically symmetric hard ellipsoids, though with a variety of sizes and axis ratios. The solute lengths along the symmetry axis, l , and diameter, w , are expressed in units of solvent width, d . An equilibration period of $(1-2) \times 10^5$ trial moves per particle was used, starting from an initial configuration where all of the molecules were orientationally aligned and positioned on a stretched fcc lattice.

The sequence of system configurations was generated using the Metropolis algorithm [43]. In some of the simulations, only a hard-core pair interaction between molecules was considered. In this case, trial orientational and translational moves for each randomly chosen particle were rejected if it resulted in overlap with any of the other particles, and accepted if there was no overlap. However, most of the calculations involved systems of particles with an additional interaction between point quadrupoles positioned at the centers of the ellipsoids. For such systems, the Metropolis algorithm is applied as follows. Trial configurations are first tested for overlap. If particles overlap, then the configuration is rejected. If the particles do not overlap, the quadrupole-quadrupole energy of the total system is calculated and compared to that of the previous configuration. If $\Delta E < 0$, then the move is accepted; if $\Delta E > 0$, then the configuration is accepted with a probability given by $e^{-\Delta E/k_B T}$. The maximum displacements and rotations were chosen to contribute approximately equally to the likelihood that a particle move would be rejected, and to yield an overall acceptance ratio in

the range of 40–60 % in order to achieve equilibrium as rapidly as possible.

The solvent-solvent quadrupolar pair potential was calculated using the following relation for the interaction between two axially symmetric quadrupoles [41]:

$$u_{QQ} = \frac{3}{4} \left(\frac{Q_{zz}^{(1)} Q_{zz}^{(2)}}{4 \pi \epsilon_0 r^5} \right) [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 + 2 \cos^2 \theta_{12} + 35 \cos^2 \theta_1 \cos^2 \theta_2 - 20 \cos \theta_1 \cos \theta_2 \cos \theta_{12}], \quad (28)$$

where θ_1 and θ_2 are the angles between the quadrupole symmetry axis and the displacement vector between the point quadrupoles, and θ_{12} is the angle between the two quadrupole symmetry axes. The contribution to the EFG at the site of the solute due to a solvent point quadrupole moment $Q_{\mu\nu}^{(v)}$ was calculated using the following expression:

$$\begin{aligned} F_{\mu\nu} &\equiv \nabla_\mu E_\nu = -\nabla_\mu \nabla_\nu \phi \\ &= \frac{1}{r^5} [-2Q_{\mu\nu}^{(v)} + 10Q_{\alpha\nu}^{(v)} \hat{r}_\alpha \hat{r}_\mu + 10Q_{\mu\alpha}^{(v)} \hat{r}_\alpha \hat{r}_\nu \\ &\quad + 5Q_{\alpha\beta}^{(v)} \hat{r}_\alpha \hat{r}_\beta \delta_{\mu\nu} - 35Q_{\alpha\beta}^{(v)} \hat{r}_\alpha \hat{r}_\beta \hat{r}_\mu \hat{r}_\nu], \end{aligned} \quad (29)$$

where \hat{r} is a unit vector describing the orientation of the displacement between the quadrupole pair, and where we have used the Einstein summation convention for repeated indices. The solute-solvent pair potential is a function of the EFG due to the solvent:

$$u_{QQ} = -\frac{1}{3} Q_{\mu\nu} F_{\mu\nu} = -\frac{1}{3} Q_{\alpha\beta}^{(P)} \cos \theta_{\alpha\mu} \cos \theta_{\beta\nu} F_{\mu\nu}, \quad (30)$$

where $Q_{\mu\nu}$ and $Q_{\alpha\beta}^{(P)}$ are the solute quadrupole moments in the laboratory and principal axis system (PAS) frames, respectively, and $\cos \theta_{\alpha\mu}$ is the angle between the PAS α axis and the laboratory μ axis.

The total energy is obtained by summing the pair potentials over all of the particles in the system, and averaging over the sequence of configurations which are generated by the Metropolis algorithm. In certain cases for long-range interactions it is necessary to include contributions to the total energy from particles that are very widely spaced in order to minimize truncation effects. For a finite-sized simulation system, this often requires a summation over molecules in repeated images of the system. However, this greatly increases the time required to perform a simulation. In the present case, the quadrupole-quadrupole pair potential decays as r^{-5} , which was found to be sufficiently rapid to eliminate the need to perform such a lattice summation. The energy of a single molecule was calculated by summing over the pair potentials between it and all other molecules within a radius given by half the smallest dimension of the sample cell. For a density of $\rho^* = 0.42$, this corresponds to a distance of $r = 4.96d$, where d is the width of a solvent ellipsoid. When this maximum distance was doubled, the calculated energy of the system and of each of the molecules, and the EFG sampled by the solute, was found to change by $< 1\%$ for each of several different system configurations. In addition ensemble averages of various quantities of interest were not affected by increasing the sampling range.

Most of the simulations for the quadrupolar systems were performed at $Q_v^* = -\sqrt{2.5}$ and $\rho^* = 0.42$. The choice of Q_v^* falls at the lower end of a range of values ($|Q_v^*| \approx 0.75-4.0$) suitable for $T=300$ K and $d \approx 5$ Å using the results of a study which employed a simple atom-dipole method for approximating the quadrupole moment for rigid conformers of various real nematogens [19]. The use of higher values of Q_v^* was found to promote the formation of a smectic phase in the model system and was therefore avoided. Note that we neglect the axial asymmetry of the $Q_{\alpha\beta}^{(v)}$ tensor present in real molecules.

The nematic order parameter $\bar{P}_2^{(\text{nem})}$ was determined by calculating the largest eigenvalue of the following matrix:

$$\langle \mathbf{Q} \rangle = \frac{1}{N} \sum_{i=1}^N \langle \frac{3}{2} \hat{u}_i \hat{u}_i - \frac{1}{2} \mathbf{I} \rangle, \quad (31)$$

where N is the number of solvent molecules, and \hat{u}_i is a unit vector describing the orientation of the i th solvent molecule. The brackets $\langle \rangle$ denote an ensemble averaging over the sequence of configurations generated by the MC Markov process. The nematic director is given by the eigenvector corresponding to this eigenvalue. In addition to the nematic order parameter, the following functions were also calculated:

- (i) The solvent orientational distribution function $\tilde{f}(\theta)$.
- (ii) The solvent-solvent pair correlation function $g_{vv}(r^*)$.
- (iii) The second-rank solvent-solvent orientational correlation function $\bar{P}_2^{(vv)}(r^*)$ defined as follows:

$$\bar{P}_2^{(vv)}(r^*) = \frac{1}{N(N-1)} \sum_{i \neq j} \langle P_2(\cos \theta_{ij}) \rangle, \quad (32)$$

where θ_{ij} is the angle between solvent ellipsoids i and j .

- (iv) The solute orientational order parameter \bar{P}_2 .
- (v) The solute orientational distribution function $f(\theta)$.
- (vi) The average EFG tensor at the center of the solute, $\bar{F}_{\alpha\beta}$, in the frame of the nematic director.
- (vii) The solute-solvent radial distribution function $g_{uv}(r^*)$.
- (viii) The solute-solvent orientational correlation function $\bar{P}_2^{(uv)}(r^*)$, defined in a manner analogous to that for $\bar{P}_2^{(vv)}(r^*)$ above.
- (ix) The fourth-rank orientational order parameter for the distribution of solute-solvent intermolecular displacements $\bar{P}_4^+(r^*)$.

All of the measured quantities described above were calculated by averaging over typically $(8-9) \times 10^5$ configurations. In order to calculate properly all quantities that are measured with respect to the nematic director, which undergoes orientational fluctuations over the course of a simulation, the director was recalculated after every 10^1-10^2 attempted moves per particle. All calculated quantities which are functions of orientation with respect to the director were calculated for $\cos \theta$ in the range 0 – 1 in increments of 0.01. Further, the quantities which depend on the intermolecular separation r were calculated to a distance of half the minimum dimension of the sample cell (e.g., $4.96d$ for $\rho^* = 0.42$) in increments of $0.05d$. Solute and solvent orien-

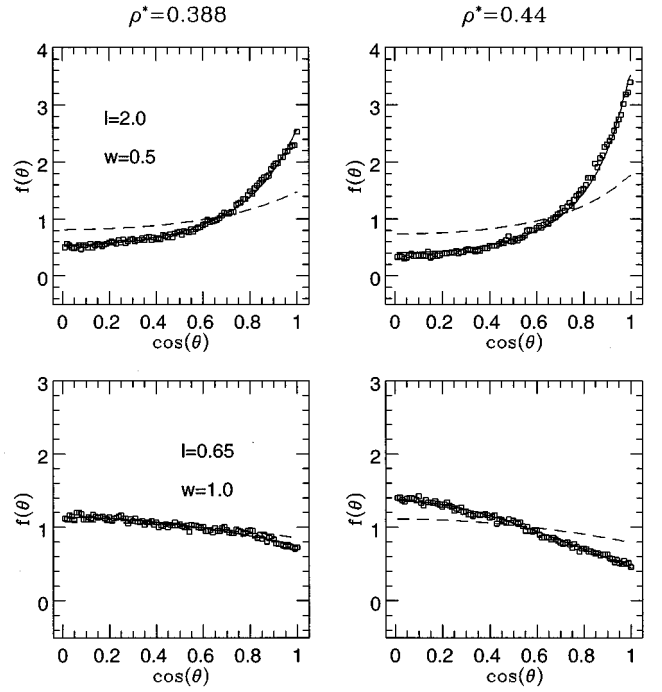


FIG. 1. Calculated and theoretical solute orientational distribution functions for hard-core systems (I). MC data (squares) and predictions from TP theory using Eq. (13) (dashed line) and Eq. (33) (solid line).

tational order parameters and EFG tensor components were calculated in 80–90 block averages of 10^4 sweeps through the system. The fluctuations of these averages were used to provide an estimate of the uncertainties of these quantities.

IV. RESULTS AND DISCUSSION

A. Hard-core system

Oriental distribution functions for four different solutes were calculated for two different densities for a system employing only hard-core interactions. The MC distributions are shown in Figs. 1 and 2. The corresponding second-rank solute orientational order parameters are listed in Table I. The variation of the distributions with solute shape and solvent density is similar to that observed in our previous MC simulation study [33]. Increasing the length of the solute results in an increase in the degree of orientational ordering. This is evident in Fig. 2, which shows distributions for solutes with dimensions of $l=5.0$ and $w=1.0$, and $l=2.0$ and $w=1.0$. Further, increasing the solvent density, and therefore the degree of solvent orientational order, leads to a corresponding increase in solute orientational order. Note that the oblate solute with dimensions of $l=0.65$ and $w=1.0$ prefers to orient with its symmetry axis perpendicular to the nematic director, resulting in a distribution maximum at $\theta=90^\circ$ and a negative order parameter.

We use the results of these simulations to test the predictions of the TP theory, assuming that the mean-field potential is due to hard body interactions given by Eq. (11) or equivalently by Eq. (13). The orientation-dependent excluded volume $V_{\text{ex}}(\omega, \omega')$, which for axially symmetric ellipsoids is a function of only the angle between the symmetry axes, was calculated through a numerical integration over the magni-

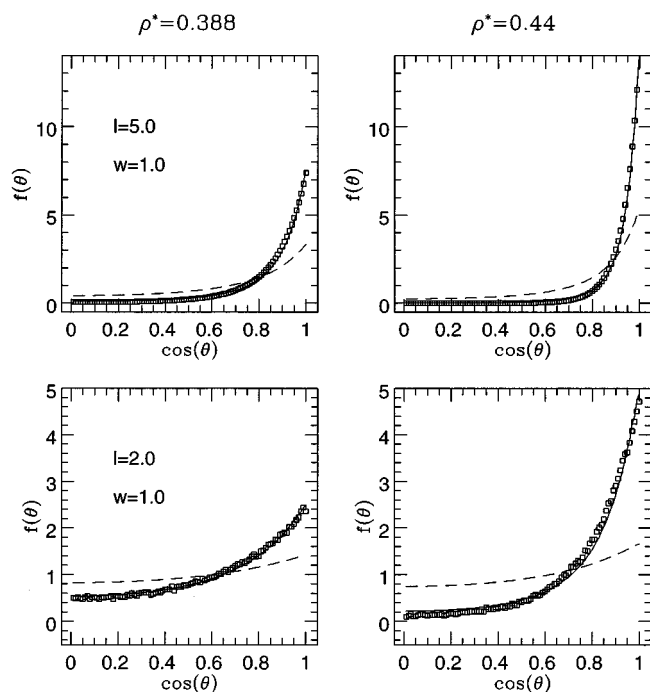


FIG. 2. Calculated and theoretical solute orientational distribution functions for hard-core systems (II). MC data (squares) and predictions from TP theory using Eq. (13) (dashed line) and Eq. (33) (solid line).

tude and direction of the solute-solvent intermolecular vector. The results for the case of identical 5:1 ellipsoids were consistent with those reported by Tjipto-Margo and Evans, [44]. Note that the potential of Eqs. (11) and (13) is expressed in terms of the solvent orientational distribution function $\tilde{f}(\omega)$. Thus, in order to calculate the solute distribution, we use the solvent distribution calculated in the MC simulation. Also note that in the study of Terzis and Photinos, the mean-field potentials were rewritten in terms of the solvent order parameters $\bar{P}_2^{(\text{nem})}$ and $\bar{P}_4^{(\text{nem})}$, with higher order contributions neglected. The values of these quantities had not been reported previously, and thus had to be estimated; values were chosen in order to yield calculated order

parameters to be consistent with experimentally measured order parameters for several molecules. Clearly, the MC technique provides a superior method to test the approximations of the theory.

The calculated theoretical distribution functions are shown as the dashed curves overlaid on the plots of the MC distributions in Figs. 1 and 2 for the four different solutes at densities of $\rho^*=0.388$ and 0.44 . In all cases the TP theory drastically underestimates the degree of orientational order observed in these hard-core systems. This contrast is further illustrated by comparing the theoretical and calculated second rank order parameters \bar{P}_2 in Table I. A notable case is that of the solute which is identical to the solvent particles ($l=5$, and $w=1$). In this case, the MC orientational distribution function of the solute is identical to the solvent distribution which was used in the calculation of the theoretical solute distribution function; thus the very poor agreement between theory and simulation highlights the lack of internal self-consistency of the theory. Clearly, the hard-core component of the TP mean-field potential given by Eq. (11) gives an inadequate description of orientational ordering for hard-core systems.

The flaw in the TP theory must be due to the approximation of neglecting solvent-solvent correlations, which is expressed in Eq. (2). This is not a surprising finding given the high density of the nematic phase, coupled with the short-range nature of the interaction. It is analogous to the poor quantitative predictions of Onsager theory, which accounts for only two-particle correlations, when applied to hard particles of realistic length-width ratios. In the study by Tjipto-Margo and Evans [44], an additional term involving the third virial coefficient (which accounts for three-body correlations) in the expression for the free energy for a system of hard ellipsoids with a dimension ratio of 5:1 was included; this approach yielded an adequate quantitative description of nematogen ordering. Similarly, the TP theory requires a more careful treatment of many-particle correlations, beyond the consideration of solute-solvent effects alone, in order to provide a reasonable description of solute orientational behavior. Such a modification, however, may be difficult to incorporate into the framework of the theory.

TABLE I. MC and theoretical solute order parameters for a hard-core system.

| ρ^* | l^a | w^a | \bar{P}_2 (MC) | \bar{P}_2 (Th. I) ^b | \bar{P}_2 (Th. II) ^c | q^d | $\bar{P}_2^{(\text{nem})}$ |
|----------|-------|-------|------------------|----------------------------------|-----------------------------------|-------|----------------------------|
| 0.388 | 0.65 | 1.0 | -0.05(1) | -0.03 | -0.05 | 1.8 | 0.627(4) |
| | 2.0 | 1.0 | 0.24(1) | 0.08 | 0.24 | 2.8 | 0.626(4) |
| | 2.0 | 0.5 | 0.23(1) | 0.08 | 0.24 | 2.6 | 0.629(4) |
| | 5.0 | 1.0 | 0.63(1) | 0.31 | 0.61 | 2.1 | 0.626(4) |
| 0.44 | 0.65 | 1.0 | -0.13(1) | -0.04 | -0.12 | 3.2 | 0.814(4) |
| | 2.0 | 1.0 | 0.50(1) | 0.12 | 0.48 | 3.9 | 0.811(4) |
| | 2.0 | 0.5 | 0.34(1) | 0.12 | 0.34 | 2.5 | 0.810(4) |
| | 5.0 | 1.0 | 0.81(1) | 0.46 | 0.80 | 2.3 | 0.811(4) |

^aUnits of solvent ellipsoid width d .

^bCalculated using Eq. (11).

^cCalculated using Eq. (33).

^dFactor appearing in Eq. (33).

A simple alternative approach to improving the TP theory was provided in a recent study by Terzis *et al.* [45]. In this study, the TP theory was used to analyze the orientational ordering of a series of cyclic aliphatic solutes in a nematic solvent. The principal advantage of using these particular solutes is that they have essentially vanishing electrostatic multipole moments, and thus the principal ordering mechanism should be the short-range anisotropic component of the solute-solvent pair potential. Thus Eq. (11) [or, equivalently, Eq. (13)] was used as the theoretical solute mean-field potential. Note that the solvent orientational distribution cannot be determined from the NMR experiments, and thus the potential was rewritten in terms of a spherical harmonic expansion, with solvent order parameters constituting the expansion coefficients, which was truncated to second rank. In the analysis, the parameter $p \equiv \rho v \bar{P}_2^{(\text{nem})}$, where v is the volume of the nematogen, was treated as an adjustable parameter in order to fit the solute order parameters. As expected, it was found that p was independent of the properties of the solute (to within 10%). In addition, it was found that p actually exceeded unity over a significant temperature range, a result that is clearly forbidden by the definition of this parameter. This result is clearly a consequence of neglecting the solvent-solvent correlations in the derivation of the theoretical potential. Further, it was suggested that the effect of neglecting the solvent-solvent correlations in the theory can be compensated for by considering v to be an effective nematogen volume, which is clearly larger than the true volume. The usefulness of the theory for predicting the orientational behavior of solutes was supported by the observation that the value of p was roughly solute independent at a fixed temperature for a particular nematic solvent. Thus the theory should predict the orientational behavior of an arbitrary solute, if the order parameters of any one solute are known, under the assumption that short-range repulsive forces are the dominant orienting mechanism.

We have analyzed further our results for the hard-core system by employing a modified form of the potential of Eq. (13) given by the following equation:

$$U_{\text{HC}}(\omega)/k_B T = q\rho \int d\omega' V_{\text{ex}}(\omega, \omega') \tilde{f}(\omega'), \quad (33)$$

where q is a factor introduced to compensate for the neglect of solvent-solvent correlations, related to the parameter p described above. Specifically, it can be considered to be the ratio of an effective solvent packing fraction to the true packing fraction. The new fits of the MC solute distribution functions are shown as the solid curves in Figs. 1 and 2. Changing the packing fraction through the optimization of q clearly results in a dramatically improved prediction of the distribution functions. This is also clear from the values of the order parameters which correspond to these fits, which are listed in Table I. The fitted values of q are also shown in the table. In all cases, it was found that the effective packing fraction was significantly greater than the true packing fraction (i.e., $q > 1$), a result which is consistent with the results of the experimental study by Terzis *et al.* [45]. We note, however, that the range of values of the effective packing fraction for each density for the four solutes varies more widely than was found in that study where the deviations among solutes did

not exceed 10%. This may be due to the fact that the solute shapes used in the MC simulations of this study were chosen to be significantly different, while those used in the study of Terzis *et al.* were (necessarily) structurally similar. It is also possible that molecular flexibility of both the solvent and solute molecules of the experimental system may improve the consistency of the fits among the solutes. In any case, the magnitude of the variations in the effective packing fractions observed in the present study suggest that the predictive power of the hard-core component of the TP mean-field potential may be limited.

B. Quadrupolar systems

Table II lists the \bar{P}_2 and \bar{F}_{ZZ}^* calculated for simulations employing a wide variety of solute shapes and quadrupole moments. The nematic solvent was characterized by a reduced density of $\rho^* = 0.42$, and by quadrupole moments with values of $Q_v^* = -\sqrt{2.5}$. The nematic order parameter was found to be $\bar{P}_2^{(\text{nem})} = 0.76 \pm 0.01$, with some minor variations between systems with different solutes; specific values are listed in Table II. Further, the table shows the theoretical \bar{F}_{ZZ}^* calculated using Eq. (25) and theoretical predictions of \bar{P}_2 for spherical solutes using the reduced mean-field potential of Eq. (26) of the EL theory. Note that \bar{F}_{ZZ}^* calculated in both the MC simulations and by EL theory is proportional to $Q_{zz}^{(v)}$ [see Eqs. (25) and (29)]. Thus the sign of \bar{F}_{ZZ}^* is determined by the sign of $Q_{zz}^{(v)}$, which in the present calculations was taken to be $Q_{zz}^{(v)} < 0$. Using a positive value of $Q_{zz}^{(v)}$ simply reverses the sign of \bar{F}_{ZZ}^* but otherwise has no effect on the calculated quantities.

The most striking result is the strong dependence of \bar{F}_{ZZ}^* on the shape and quadrupole moment of the solute. This is in contrast to the solute-independent model put forward by Burnell and co-workers. For the case of spherical solutes, \bar{F}_{ZZ}^* increases in magnitude for increasing $|Q_u^*|$, though it is approximately symmetric with respect to changing the sign of Q_u^* , since the sign of \bar{F}_{ZZ}^* is consistently positive. This is clearly not the case for the nonspherical solutes where the shape anisotropy breaks the symmetry and \bar{F}_{ZZ}^* undergoes concomitant change in sign with Q_u^* . Thus, for the oblate solute, $\bar{F}_{ZZ}^* < 0$ for $Q_u^* Q_v^* < 0$, and $\bar{F}_{ZZ}^* > 0$ for $Q_u^* Q_v^* > 0$. The trend is the reverse for the various prolate solutes.

The dependence of \bar{F}_{ZZ}^* on Q_u^* is qualitatively consistent with the behavior of the measured orientational order parameters \bar{P}_2 in the context of a mean-field EFG-quadrupole moment interaction given by Eqs. (22) or (26). In the case of the spherical solutes, the consistently positive \bar{F}_{ZZ}^* is predicted successfully by Eq. (26) to give $\bar{P}_2 > 0$ for $Q_u^* > 0$ and $\bar{P}_2 < 0$ for $Q_u^* < 0$ (for the present case where $Q_v^* < 0$). This is also consistent with the expected behavior of \bar{P}_2 based on a consideration of the quadrupole-quadrupole pair potential alone. For axially symmetric quadrupole moments of the same sign, the minimum energy orientational configuration is a perpendicular arrangement of the symmetry axes; thus a negative order parameter is expected. For quadrupole moments of opposite signs, a parallel configuration corresponds to the lowest energy, and thus a positive \bar{P}_2 is predicted.

TABLE II. EFG and order parameters for several solutes at $\rho^*=0.42$ and $(Q_v^*)^2=2.5$.

| Shape | Dimensions | $Q_u^*Q_v^*$ ^a | \bar{F}_{ZZ}^* (MC) ^a | \bar{F}_{ZZ}^* (Th) ^b | \bar{P}_2 (MC) | \bar{P}_2 (Th) ^c | $\bar{P}_2^{(nem)}$ |
|-----------|----------------------|---------------------------|------------------------------------|------------------------------------|------------------|-------------------------------|---------------------|
| Spherical | $l=1.0$ $w=1.0$ | -2.5 | 1.8(2) | 1.5 | 0.26(2) | 0.50 | 0.749(3) |
| | | -2.0 | 1.0(1) | 0.9 | 0.15(2) | 0.19 | 0.750(3) |
| | | -1.5 | 0.5(1) | 0.5 | 0.07(1) | 0.08 | 0.761(2) |
| | | 0.0 | 0.05(3) | 0.15 | 0.01(1) | 0.0 | 0.751(3) |
| | | 1.5 | 0.5(1) | 0.4 | -0.03(2) | -0.05 | 0.756(2) |
| | | 2.0 | 1.4(1) | 1.4 | -0.10(2) | -0.22 | 0.756(2) |
| Spherical | $l=0.75$ $w=0.75$ | 2.5 | 2.2 (2) | 2.4 | -0.16(2) | -0.32 | 0.758(2) |
| | | -1.5 | 3.8(2) | 3.9 | 0.29(2) | 0.59 | 0.757(2) |
| | | -1.0 | 1.1(1) | 1.1 | 0.09(1) | 0.12 | 0.754(2) |
| | | 0.0 | 0.04(3) | 0.07 | 0.01(1) | 0.0 | 0.761(2) |
| | | 1.0 | 1.8(1) | 1.7 | -0.06(1) | -0.14 | 0.757(2) |
| | | 1.5 | 5.4(3) | 4.9 | -0.19(2) | -0.36 | 0.757(2) |
| Oblate | $l=0.65$ $w=1.0$ | -1.5 | -0.8 (1) | -0.9 | -0.11(1) | | 0.759(2) |
| | | -0.75 | -0.32(4) | -0.39 | -0.12(1) | | 0.751(2) |
| | | 0.0 | -0.01(3) | -0.05 | -0.09(1) | | 0.756(2) |
| | | 0.75 | 2.1(1) | 2.0 | -0.14(1) | | 0.761(2) |
| | | 1.5 | 11.8(4) | 15.5 | -0.37(2) | | 0.752(2) |
| Prolate | $l=2.0$ $w=1.0$ | -2.5 | 2.7 (1) | 3.0 | 0.56(2) | | 0.762(2) |
| | | -1.5 | 1.0 (1) | 1.0 | 0.39(3) | | 0.758(2) |
| | | 0.0 | -0.01(3) | -0.02 | 0.30(2) | | 0.753(2) |
| | | 1.5 | -0.39(3) | -0.39 | 0.37(2) | | 0.768(2) |
| | | 2.5 | -0.66(4) | -0.70 | 0.40(2) | | 0.761(2) |
| Prolate | $l=3.0$ $w=1.0$ | -2.5 | 2.9(1) | 3.0 | 0.67(2) | | 0.761(2) |
| | | 0.0 | 0.00(3) | 0.08 | 0.55(2) | | 0.756(3) |
| | | 2.5 | -1.03(4) | -1.36 | 0.66(2) | | 0.763(2) |
| Prolate | $l=4.0$ $w=1.0$ | -2.5 | 3.3(2) | 4.0 | 0.74(2) | | 0.760(2) |
| | | 0.0 | 0.01(3) | 0.01 | 0.66(2) | | 0.761(2) |
| | | 2.5 | -1.1(1) | -1.2 | 0.73(2) | | 0.762(3) |
| Prolate | $l=5.0$ $w=1.0$ | -2.5 | 3.5 (1) | 4.6 | 0.81(1) | | 0.768(2) |
| | | 0.0 | -0.04(3) | -0.14 | 0.80(1) | | 0.772(2) |
| | | 2.5 | -1.16(5) | -1.50 | 0.78(2) | | 0.763(2) |

^aCalculated using $Q_{zz}^{(v)} = -\sqrt{2.5} < 0$; using $Q_{zz}^{(v)} = +\sqrt{2.5} > 0$ simply reverses the sign of \bar{F}_{ZZ}^* .

^bCalculated using Eq. (25).

^cCalculated using Eq. (26).

The asymmetry of \bar{F}_{ZZ}^* for the nonspherical solutes is also consistent with the behavior of the calculated orientational order parameters \bar{P}_2 , referenced with respect to the systems with $Q_u^*=0$. For the case of the oblate solute, the negative \bar{P}_2 is enhanced by the positive \bar{F}_{ZZ}^* , which is present for $Q_u^*Q_v^*>0$. Again, this is consistent with the expectation based on the orientation dependence of the quadrupole-quadrupole pair potential. However, a somewhat surprising result is the (minor) enhancement of the negative \bar{P}_2 for the case of opposite signs of solvent and solute quadrupole moments, where the lowest pair potential energy configuration corresponds to a parallel arrangement of the quadrupole symmetry axes. While the corresponding case for spherical solutes gave rise to an alignment of the solute symmetry axis

along the nematic director, the nature of the shape anisotropy for the oblate solute appears to frustrate that outcome.

The analogous situation is present for the various prolate solutes. In this case, the expected enhancement of the positive value of \bar{P}_2 , relative to the case of $Q_u^*=0$, for $Q_u^*Q_v^*<0$ is observed, as well as an unexpected enhancement of \bar{P}_2 for $Q_u^*Q_v^*>0$. Again, the increase in solute orientational ordering with $|Q_u^*Q_v^*|$, regardless of the sign of $Q_u^*Q_v^*$, is consistent with the change in sign of \bar{F}_{ZZ}^* .

In the case of the large prolate solute, with dimensions equal to those of the solvent ellipsoids ($l=5.0$, $w=1.0$), \bar{F}_{ZZ}^* has a similar dependence on $Q_u^*Q_v^*$ relative to the case of the smaller prolate ellipsoid. Note, however, that the orientational ordering is not significantly affected by the details

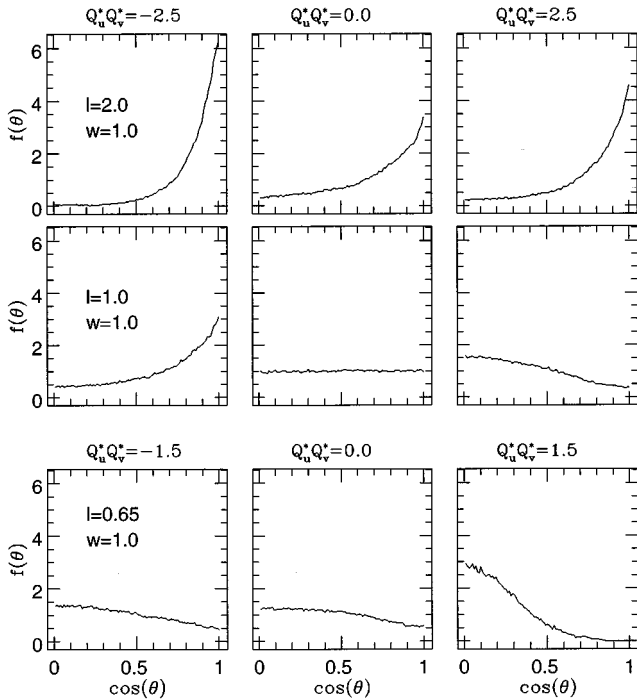


FIG. 3. Solute orientational distribution functions at $(Q_v^*)^2 = 2.5$ and $\rho^* = 0.42$.

of the electrostatic interactions. Thus orientational ordering of highly elongated particles in a dense nematic phase appears to be dominated by entropic considerations, in keeping with the belief that molecular shape anisotropy, in conjunction with short-range repulsive forces, is the dominant ordering mechanism for nematics.

The full orientational distribution functions for three solutes are plotted for $Q_u^* Q_v^* = 0, \pm 2.5$ or $0, \pm 1.5$ in Fig. 3. The trends present in the behavior of the \bar{P}_2 for each of the solutes is mirrored by the behavior of the distributions. Only in the case of the spherical solute is the orientational ordering consistent with an interaction between the solute quadrupole moment and a \bar{F}_{ZZ}^* of a constant sign. The behavior of the solute-solvent orientational correlation functions $\bar{P}_2^{(uv)}(r^*)$ for the same solutes, shown in Fig. 4, provides some additional insight into the perturbing influence of the quadrupole-quadrupole pair interactions on the ordering of the solutes. Note that in the limit of $r^* \rightarrow \infty$, $\bar{P}_2^{(uv)}(r^*) = \bar{P}_2 \bar{P}_2^{(\text{nem})}$. Thus the long-range limit of these functions provides a measure of the degree of solute orientational order. For all cases, except that of the spherical solute with $Q_u^* = 0$, there are both short- and long-range orientational correlations. In the case of the spherical solute, both long- and short-range correlations have the same pattern: enhancement of parallel configurations for solute and solvent quadrupole moments of the opposite sign, and enhancement of perpendicular configurations for quadrupole moments of the same sign. Note that the short-range, correlations are indeed very short range, as they vanish within approximately one solvent ellipsoid width d from the nearest approach distance.

The case of the prolate solute is more interesting. While oppositely signed solute and solvent quadrupole moments correspond to an enhancement of both short- and long-range parallel configurations, quadrupole moments of the same

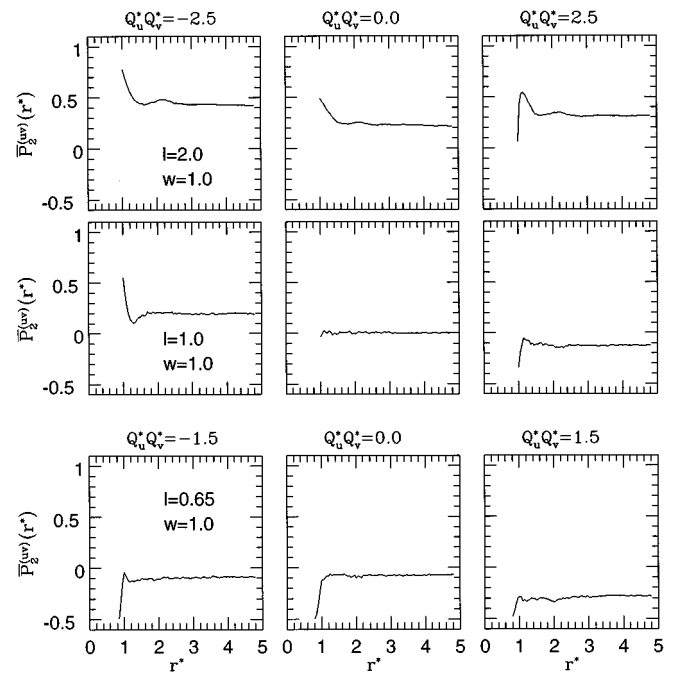


FIG. 4. Solute-solvent orientational correlation functions for $(Q_v^*)^2 = 2.5$ and $\rho^* = 0.42$.

sign lead to a slight enhancement of long-range parallel configurations, but a significant reduction of short-range parallel configurations. The latter feature is more in keeping with expectations based on the orientation-dependence of the quadrupole-quadrupole pair potential. In the case of the oblate solute, there is no noticeable effect of the quadrupole-quadrupole pair potential on the short-range orientational correlations.

Figure 5 illustrates the effect of increasing solute length on the order parameter \bar{P}_2 for three different values of the solute quadrupole moment: $Q_u^* Q_v^* = 0, \pm 2.5$. The width of all of the solutes is fixed to that of the solvent, $w = 1$. The increase in the degree of orientational ordering with increasing length, regardless of the value of the quadrupole moment, is clear. The unexpected enhancement of orientational ordering described above for prolate solutes with $Q_u^* Q_v^* = +2.5$ relative to the case where $Q_u^* Q_v^* = 0$ is also

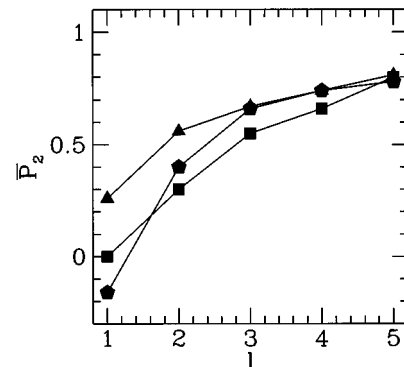


FIG. 5. Solute orientational order parameter vs solute length with $w = 1.0$. $Q_u^* Q_v^* = -2.5$ (triangles), 0.0 (squares), and 2.5 (pentagons).

TABLE III. Experimental order parameters for three solutes.

| Solute | Q_{zz} ^a | \bar{P}_2 ^b | | |
|-------------------|------------------------|--------------------------|------------------|-------------------|
| | | EBBA ^c | 55% ^d | 1132 ^e |
| dideuterium | 0.649 | -0.009 65 | -0.000 82 | 0.007 31 |
| benzene | -7.8(2.2) ^f | -0.1157 | -0.1756 | -0.2519 |
| hexafluorobenzene | 9.5 ^g | -0.3144 | -0.2280 | -0.2144 |
| acetylene | 5.5(2.5) ^h | -0.0585 | 0.1123 | 0.1912 |

^aUnits of 10^{-26} esu cm².

^bFrom Ref. [12].

^c $\bar{F}_{ZZ} = -6.42 \times 10^{11}$ esu for D₂.

^d $\bar{F}_{ZZ} = 0.0$ esu for D₂.

^e $\bar{F}_{ZZ} = 6.07 \times 10^{11}$ esu for D₂.

^fAverage value of those reported in Refs. [47] and [48].

^gFrom Ref. [49].

^hAverage value of those reported in Refs. [50] and [51].

evident. Finally, it is interesting to note that the effects of the quadrupolar interactions on solute ordering gradually diminish as the dimensions of the solute approach those of the nematogen. Clearly, the effects of the hard-core interactions increasingly dominate the ordering with increasing shape anisotropy. In the case where the solvent and solute dimensions are identical, the quadrupolar interactions have a negligible influence.

At this point, it is instructive to compare qualitatively the results of the simulations with certain previous experimental results. Table III lists the values of \bar{P}_2 for D₂, benzene, hexafluorobenzene, and acetylene measured in three different liquid crystals. The EFG has been measured for D₂ and HD in these nematics and was found to be positive for Merck ZLI 1132, zero for the 55 wt % ZLI 1132-EBBA mixture and negative for EBBA [8,46]. Further, benzene is known to have a large negative quadrupole moment, while hexafluorobenzene has a large positive value; approximate values are listed in the table. The magnitude of the negative value of \bar{P}_2 for benzene was found to increase with increasing \bar{F}_{ZZ} , while the opposite trend was observed for hexafluorobenzene. This behavior can be explained by the interaction of the molecular quadrupole moments interacting with an external \bar{F}_{ZZ} which has a sign that is *consistent* with that measured by molecular hydrogen for the three nematics. The values of orientational order parameters of acetylene are likewise consistent with this solute-independent mean-field prediction. In particular, note the negative value of \bar{P}_2 for acetylene in EBBA, a feature which is not easily rationalized except by an interaction between its positive Q_{zz} with a negative \bar{F}_{ZZ} . Further, note that benzene and hexafluorobenzene have approximately the same shape, despite the large difference in quadrupole moments. Thus the differences in \bar{P}_2 for the two molecules in the same liquid crystal likely arise principally from the difference in quadrupole moments. Again, the trend is consistent with a mean-field interaction between a quadrupole moment and a \bar{F}_{ZZ} with a sign which is independent of the solute Q_{zz} : the magnitude of the negative \bar{P}_2 is enhanced for $Q_{zz}\bar{F}_{ZZ} < 0$, and reduced for $Q_{zz}\bar{F}_{ZZ} > 0$, where, again, we use values of \bar{F}_{ZZ} measured using D₂. The slightly larger magnitude of \bar{P}_2 of hexafluorobenzene in the 55% mixture (where $\bar{F}_{ZZ} = 0$), compared to that of benzene, is probably due to the fact that hexafluorobenzene is slightly more oblate than benzene. To summarize, certain key experimental results strongly suggest that molecules of very different shapes and quadrupole moments interact with an average \bar{F}_{ZZ} which, at the very least, has the same sign.

Clearly, the experimental results conflict with the results of the present MC simulations, which employ the simple quadrupole-quadrupole potential to approximate the electrostatic interaction between molecules. As stated earlier, for example, the oblate solute in the simulations samples an average \bar{F}_{ZZ} whose sign was directly proportional to the sign of the solute Q_u^* which was further manifested in an enhancement of $|\bar{P}_2|$ for increasing $|Q_u^* Q_v^*|$ relative to the case of $Q_u^* = 0$ independent of the sign of $Q_u^* Q_v^*$. At this time, we cannot pinpoint precisely the origin of this sharply contradictory behavior, but it is very likely a result of using such a highly simplified form for the electrostatic pair potential. At short range, the convergence of the multipole expansion is very slow. Thus, in dense systems, an interaction between point quadrupoles may be a very poor approximation, and produce the kind of artifacts observed here with very specific molecular shapes and forms of electrostatic interactions. A significantly improved model of electrostatic interactions may be required to reproduce the qualitative trends observed in experimental studies. This consideration is important with regard to any theory of solute orientational order which uses such a simplified model for the pair potential.

The EL theory has been applied to analyze the present results. Equations (25) and (26) were used to calculate values of \bar{F}_{ZZ}^* and \bar{P}_2 . However, note that the calculation of these averages requires $\bar{P}_2^{(\text{nem})}$, $g_{uv}(r^*)$, and $\bar{P}_4^+(r^*)$, quantities which also must be calculated in the MC simulations. Thus the ‘‘theory’’ simply provides a prediction of the relationship between various quantities that may be measured for the system, rather than a theory which requires exclusively external system parameters. Thus, it is not of a form which may be used to study real nematic systems using NMR spectroscopy, for example, since $g_{uv}(r^*)$ and $\bar{P}_4^+(r^*)$ are not measurable with this technique.

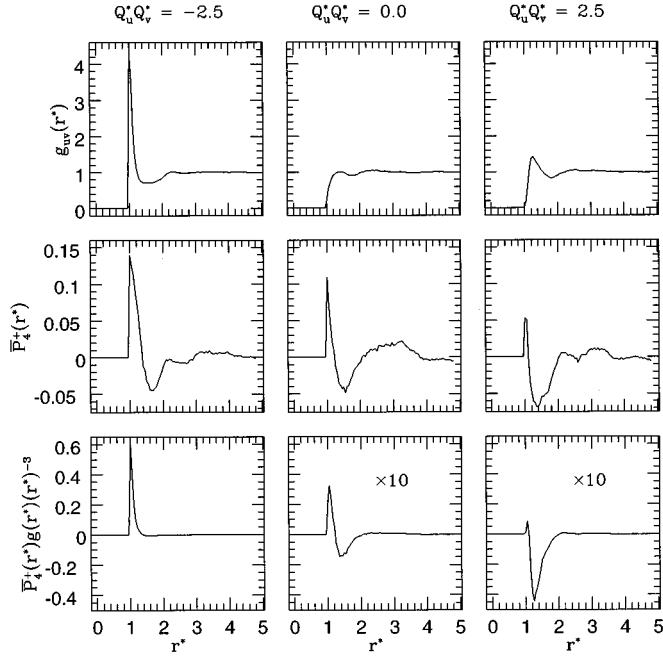


FIG. 6. Solute-solvent distribution functions for solute with dimensions of $l=2.0$ and $w=1.0$ at $\rho^*=0.42$ and $(Q_v^*)^2=2.5$.

The results of the predictions of \bar{F}_{ZZ}^* and \bar{P}_2 are summarized in Table II along with the values measured in the MC simulations. Note that \bar{P}_2 can only be calculated for spherical solutes, since the nonspherical solutes experience an additional orienting mechanism due to the shape anisotropy coupled with the short-range repulsive forces. The theoretical predictions of \bar{F}_{ZZ}^* are consistently good for all solute shapes and quadrupole moments. This is true for both the signs and magnitudes of \bar{F}_{ZZ}^* . Considering this point, we

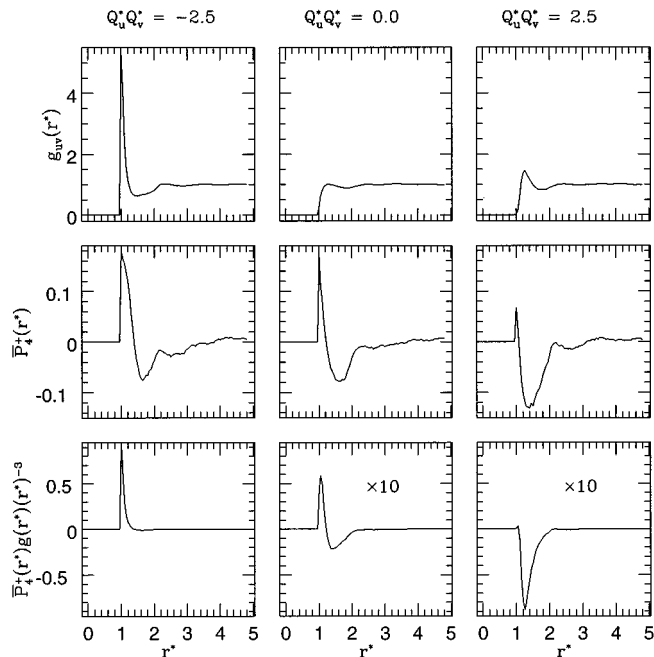


FIG. 7. Solute-solvent distribution functions for solute with dimensions of $l=5.0$ and $w=1.0$ at $\rho^*=0.42$ and $(Q_v^*)^2=2.5$.

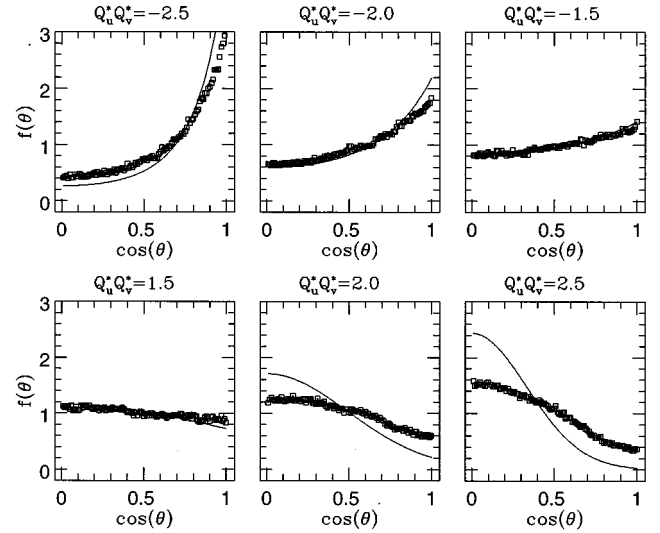


FIG. 8. MC and theoretical orientational distribution functions for spherical solutes with $(Q_v^*)^2=2.5$ and $\rho^*=0.42$.

may gain some insight into the dependence of \bar{F}_{ZZ}^* on solute properties by investigating more closely the results in the context of the theory.

In Figs. 6 and 7 we show the three solvent-solute pair distribution functions $g_{uv}(r^*)$, $\bar{P}_4^+(r^*)$, and $\bar{P}_4^+(r^*)g(r^*)(r^*)^{-3}$. Note that both the mean-field potential $U^*(\theta)$ [Eq. (24)] and \bar{F}_{ZZ}^* [Eq. (25)] are directly proportional to the latter function. Figure 6 shows the distribution functions for a prolate solute ($l=2$, $w=1$) for $Q_u^* Q_v^*=0, \pm 2.5$. For a zero quadrupole moment, there is only a vague shell structure visible in $g_{uv}(r^*)$, while there is a very strong enhancement in minimum-distance positional correlation for $Q_u^* Q_v^*=-2.5$ and a smaller enhancement at $Q_u^* Q_v^*=2.5$. The strong peak for $Q_u^* Q_v^*=-2.5$ is consistent with a strong minimum in the quadrupole-quadrupole pair potential for parallel configurations between axially symmetric quadrupoles of opposite signs. The $\bar{P}_4^+(r^*)$ distribution also undergoes noticeable changes with varying $Q_u^* Q_v^*$: increasing $Q_u^* Q_v^*$ results in a decrease in the minimum-distance positive peak and a deepening of the negative “well” to the right of this peak. These effects result in significantly different $\bar{P}_4^+(r^*)g(r^*)(r^*)^{-3}$ functions. Clearly, integration of the functions results in a $\bar{F}_{ZZ}^* > 0$ for $Q_u^* Q_v^*=-2.5$, $\bar{F}_{ZZ}^* < 0$ for $Q_u^* Q_v^*=2.5$, and a near-vanishing \bar{F}_{ZZ}^* for $Q_u^* Q_v^*=0.0$. The results for the longer prolate ellipsoid ($l=5$, $w=1$), shown in Fig. 7, are virtually identical. Thus changes in the \bar{F}_{ZZ}^* arise from changes in the structure of the solvent in the vicinity of the solute as a result of changes in the solute properties.

The theoretical predictions of \bar{P}_2 for the spherical solutes listed in Table II are generally poor, and deviate from the measured values typically by a factor of 2. This result is somewhat surprising given the accuracy of the calculated \bar{F}_{ZZ}^* , whose theoretical expression [Eq. (25)] is defined by the mean-field potential [Eq. (26)] which is used to calculate \bar{P}_2 . At the very least, however, the signs of the order parameters are accurately predicted. A comparison of the calcu-

TABLE IV. EFG and order parameters for several solutes at $\rho^*=0.39$ and $(Q_v^*)^2=2.5$.

| Shape | Dimensions | $Q_u^*Q_v^*$ ^a | \bar{F}_{ZZ}^* (MC) ^a | \bar{F}_{ZZ}^* (Th) ^b | \bar{P}_2 (MC) | \bar{P}_2 (Th) ^c | $\bar{P}_2^{(\text{nem})}$ |
|-----------|--------------------|---------------------------|------------------------------------|------------------------------------|------------------|-------------------------------|----------------------------|
| Spherical | $l=1.0$ $w=1.0$ | -2.5 | 1.8(1) | 1.2 | 0.26(2) | 0.34 | 0.637(4) |
| | | -1.5 | 0.29(5) | 0.29 | 0.04(2) | 0.04 | 0.645(4) |
| | | 0.0 | 0.04(3) | 0.05 | 0.01(1) | 0.0 | 0.641(6) |
| | | 1.5 | 0.43(6) | 0.35 | -0.01(1) | -0.05 | 0.622(7) |
| | | 2.5 | 1.5(2) | 1.5 | -0.09(2) | -0.18 | 0.636(4) |
| Prolate | $l=2.0$ $w=1.0$ | -2.5 | 2.0(1) | 1.1 | 0.44(2) | | 0.638(4) |
| | | -1.5 | 0.63(5) | 0.45 | 0.30(2) | | 0.636(4) |
| | | 0.0 | 0.01(2) | 0.06 | 0.23(2) | | 0.639(4) |
| | | 1.5 | -0.33(3) | -0.21 | 0.25(2) | | 0.657(5) |
| | | 2.5 | -0.48(4) | -0.30 | 0.29(2) | | 0.635(2) |

^aCalculated using $Q_{zz}^{(v)} = -\sqrt{2.5} < 0$; using $Q_{zz}^{(v)} = +\sqrt{2.5} > 0$ simply reverses the sign of \bar{F}_{ZZ}^* .

^bCalculated using Eq. (25).

^cCalculated using Eq. (26).

lated and theoretical solute orientational distribution function for one spherical solute ($l=w=1$) is shown in Fig. 8. Note that the accuracy of the predicted curves appears to be poorer, as the magnitude of the solute quadrupole moment increases. This discrepancy between the degree of orientational ordering calculated in theory and simulation suggests that the mathematical approximations employed in the EL theory may be too severe to yield a useful and accurate theory for solute orientational order. It is because of these approximations, which also affect the solvent orientational order, that the solvent field gradient becomes the leading electrostatic contribution. Changing the approximations will change the form of the mean field. Given that the theoretical predictions are slightly better for weaker solute-solvent couplings for the systems studied here, it could be argued that the theory is more accurate in the limit of small solute quadrupole moments. It is interesting to note that in the case of D₂ and HD, the only solutes for which the average EFG and order parameter can be simultaneously measured experimentally, the mean-field model gives excellent predictions of the measured \bar{P}_2 . Perhaps it is significant that the solute quadrupole moments for these molecules are very small, in keeping with this argument. Unfortunately, it is very difficult to test this hypothesis using MC simulations for solutes with very weak quadrupoles: the statistical fluctuations of the measured

\bar{F}_{ZZ}^* and \bar{P}_2 rapidly become very large relative to their average values, a feature that greatly increases the statistical uncertainties of these averaged quantities.

To investigate further the details of solute orientational behavior in a nematic solvent, we have conducted simulations for solutes in a nematic solvent at a lower density, and therefore, with a lower degree of orientational order. Table IV presents results for the EFG and order parameters of spherical and prolate solutes with a variety of quadrupole moments oriented in a solvent at a reduced density $\rho^*=0.39$, and with an order parameter of $\bar{P}_2^{(\text{nem})}=0.64 \pm 0.01$. As expected, there is a significant reduction in both \bar{F}_{ZZ}^* and \bar{P}_2 as a result of the decrease of the degree of nematic ordering; otherwise, there is no qualitative difference with the results for the systems at $\rho^*=0.42$.

Finally, we consider the effects of solvent-solvent correlations on the behavior of solute average properties. Earlier, it was shown that the TP theory drastically underestimates the degree of solute orientational order in hard-core systems. The cause of this problem was the severity of the approximation neglecting solvent-solvent correlations induced by the solvent-solvent hard-body interaction. A consideration which is related to that result concerns the importance of the solvent-solvent correlations on the solute properties which

TABLE V. Comparison of MC results with and without quadrupole-quadrupole interactions between solvent ellipsoids.

| Dimensions | $Q_u^*Q_v^{*c}$ | $Q_v^*-Q_v^*$ off ^a | | | $Q_v^*-Q_v^*$ on ^b | | |
|------------|-----------------|--------------------------------|-------------|----------------------------|-------------------------------|-------------|----------------------------|
| | | \bar{F}_{ZZ}^* | \bar{P}_2 | $\bar{P}_2^{(\text{nem})}$ | \bar{F}_{ZZ}^* | \bar{P}_2 | $\bar{P}_2^{(\text{nem})}$ |
| $l=1, w=1$ | 2.5 | 2.6(2) | -0.16(2) | 0.764(2) | 2.2(2) | -0.16(2) | 0.758(2) |
| $l=2, w=1$ | 2.5 | -1.03(5) | 0.49(2) | 0.766(2) | -0.66(4) | 0.40(2) | 0.761(2) |
| $l=2, w=1$ | 0.0 | 0.07(3) | 0.32(2) | 0.765(2) | -0.01(3) | 0.29(2) | 0.763(2) |

^aSolvent-solvent quadrupole interactions turned off.

^bSolvent-solvent quadrupole interactions turned on; $Q_v^* = -\sqrt{2.5}$.

^c $Q_u^*Q_v^*$ gives the solute-solvent interaction strength.

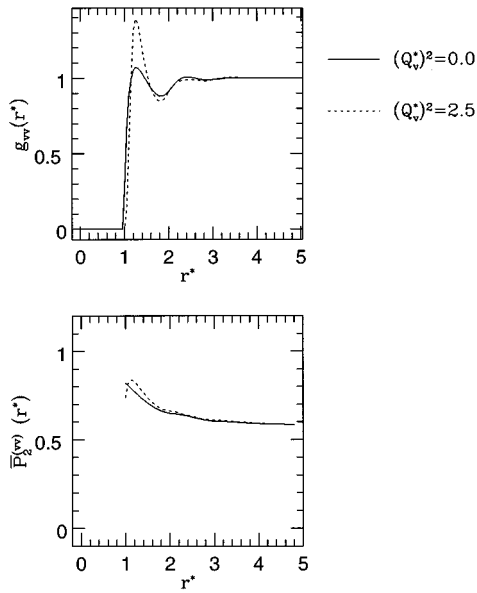


FIG. 9. Comparison of solvent-solvent pair distribution and orientational correlation functions for $(Q_v^*)^2=0$ and 2.5 at $\rho^*=0.42$.

result from the solvent-solvent electrostatic interactions. We have investigated this point by performing simulations in which solvent and solute interact both via hard-core and quadrupole-quadrupole interactions, but where solvent particles interact only with a hard-core pair potential. A comparison of the results of average solute properties with the corresponding results, where all interactions have been properly included, may provide some insight into this matter.

In Table V, we present the calculated values for \bar{F}_{ZZ}^* and \bar{P}_2 for three solutes with and without the solvent quadrupole-quadrupole interaction turned on. In the case of the spherical solute, there is a small difference in \bar{F}_{ZZ}^* and no change in \bar{P}_2 . However, for the prolate solute with $Q_u^* \neq 0$, there is a significant variation in both \bar{F}_{ZZ}^* and \bar{P}_2 . The difference is reduced by setting $Q_u^*=0$ for a solute with the same shape. Thus it appears that solvent-solvent correlations induced by solvent-solvent electrostatic interactions can indirectly affect solute properties, though in a way that clearly depends on the properties of the solute. Note that these differences do not arise from a change in the nematic order parameter: as shown in Table V, $\bar{P}_2^{(nem)}$ is not significantly affected by the presence of solvent quadrupole-quadrupole interactions of the magnitude considered here. Nevertheless, there is a significant difference in the structure of the solvent between the hard-core and the hard-core plus quadrupole systems. This difference is manifest in the solvent-solvent pair distribution and orientational correlation functions shown in Fig. 9.

V. CONCLUSIONS

In this paper, we have presented a MC simulation study of the combined effects of shape anisotropy and one specific electrostatic interaction on the orientational order of solutes in a nematic solvent. Solute and solvent molecules were constructed using a minimal model to describe pair interactions. Anisotropic short-range repulsive forces were approximated by using a hard-core potential, with axially symmetric ellip-

soids of rotation to describe the molecular shapes. Electrostatic effects were studied by incorporating an interaction between point quadrupoles embedded in the centers of the hard ellipsoids. We analyzed the results of the simulations using two current theories of orientational ordering of solutes in nematic liquid crystals.

In a purely hard-core system, solute orientational order varies in a predictable manner: increases in solute shape anisotropy and solvent density enhance the degree of ordering. The orientational distribution functions were analyzed using a theory due to Terzis and Photinos [22], which was found to underestimate the solute ordering drastically. This discrepancy is due to the complete neglect of solvent-solvent correlations in the derivation of the solute mean-field orientational potential. The severity of this approximation calls into question the results of the study which employed the theory to analyze orientational order parameters of solutes measured in previous NMR experiments. Further, the distribution functions were refit by optimizing the effective solvent packing fraction. The distributions calculated in the fits were significantly better than the original calculated distributions; in addition, the effective packing fractions were found to be consistently greater than their true values, in agreement with an experimental study by Terzis *et al.* [45]. However, unlike that study, it was found that the effective packing fractions varied significantly among solutes of different shapes, a result that calls into question the predictive power of the hard-core component of the TP mean-field potential.

In the quadrupolar systems, the relationship between the hard-core and electrostatic contributions to solute orientational ordering was investigated in detail. The behavior of the properties for a large collection of solutes of varying shapes and quadrupole moments was examined. In addition, we were particularly interested in testing the accuracy of a mean-field model proposed by Burnell and co-workers in which the interaction between the molecular quadrupole moment and a solute-independent average EFG sampled by the solute constitutes an important orientational ordering mechanism. To this end, the relationship between the measured average EFG and orientational order parameters was examined in detail. Further, a theoretical mean-field potential and average EFG can be derived using a method due to Emsley and co-workers. The theory provides a simple relationship between the solute order and various solute-solvent functions in the vicinity of the solute. This approach was found to give some insight into the solute orientational behavior.

A significant result of the simulations employing the point quadrupole electrostatic model was that the measured EFG sampled by the solute was found to be highly sensitive to the details of the properties of the solute, in contrast to the model put forward by Burnell and co-workers. In the case of non-spherical solutes, the EFG was found to experience a concomitant change in sign with the solute quadrupole moment. This result is in sharp contradiction with certain key experimental NMR results, for which it was found that the order parameters of several molecules conform to the mean-field model where the solutes interact with an EFG which, at the very least has the same sign. The origin of this discrepancy is very likely the inadequacy of using point quadrupoles for dense systems for which the convergence of the multipole expansion at short distances becomes an important consider-

ation. Thus an improved description of molecular electrostatic interactions will likely be essential in order to generate solute orientational behavior consistent with that observed experimentally.

Despite the problems with the molecular model outlined above, the observed orientational ordering was qualitatively consistent with the predictions of the mean-field model, using the measured values of the EFG for each solute individually. In addition, the EL theoretical prediction of the solute EFG, which is related to the local solvent structure, was quite accurate. The EL prediction of the orientational order of spherical solutes, for which there is only the electrostatic contribution to ordering, was qualitatively correct, though quantitatively rather poor. Thus the mathematical approximations of the EL theory appear to be too severe. Note that the theory requires a simple form for the pair potential in order to yield a simple, tractable expression for the mean-

field potential. However, as we described above, the interaction between point moments to represent electrostatic interactions was found to be inadequate for dense systems. Thus, given the combined inadequacy of both the basic electrostatic pair potential and the mathematical approximations of the theory, an accurate theoretical description of the electrostatic contributions to the orientational ordering of solutes in a nematic liquid crystal is not yet available.

ACKNOWLEDGMENTS

We would like to thank G. N. Patey for many very useful discussions and insightful suggestions. We would also like to thank C. A. de Lange and R. T. Syvitski for stimulating discussions. Financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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