Conformational energy landscapes of liquid crystal molecules

S. J. Clark; C. J. Adam; D. J. Cleaver; J. Crain

PLEASE SCROLL DOWN FOR ARTICLE

Conformational energy landscapes of liquid crystal molecules

by S. J. CLARK†, C. J. ADAM†, D. J. CLEAVER‡ and J. CRAIN*†

†Department of Physics and Astronomy, The University of Edinburgh, Edinburgh,
EH9 3JZ, Scotland, United Kingdom

‡Division of Applied Physics/Materials Research Institute,
Sheffield Hallam University, Sheffield, S1 1WB

The conformational energy landscape of the prototypical nematic liquid crystal 4-pentyl-4′-cyanobiphenyl (5CB) is studied using first principles computer modelling. It is found that the most favourable conformation occurs when the two constituent phenyl rings are inclined at an angle of 31° with respect to each other. Also, the orientation of the alkyl chain is found to have an important influence on the ring–ring torsional potential. We fit the energy surface of these coupled torsions to yield an accurate intramolecular potential for use in empirical modelling. To test the strength of the coupling between the alkyl tail and the phenyl rings and the cyano group, we also calculate potentials for the relative orientation of the phenyl rings in biphenyl and cyanobiphenyl (0CB). Our calculations are performed using density functional theory using pseudo-potentials and the generalized gradient approximation to exchange and correlation. The molecular electronic wavefunction is expanded in terms of a plane wave basis set. We compare our results with recent NMR and Gaussian-based quantum chemistry calculations where available.

1. Introduction

Computer simulation is an increasingly popular tool for the study of mesogenic behaviour. Like all modelling, however, the validity of the final results and the limit to which they may be interpreted depends on the interaction potential employed. The simplest simulation models for liquid crystals are the highly idealized lattice models, such as the Lebwohl–Lasher model [1], which can provide a useful test for various theoretical approaches, as well as being the only route currently available to device-size simulations. Another popular class of model is the hard anisotropic particle [2], which represents a generalisation of the classic hard sphere system [3]. Extensive simulations showed that such systems display nematic, smectic and columnar phases and that, therefore, the associated transitions can be purely entropically driven. The need to explore the effects of generic interaction types on phase stability has led to development of liquid crystal models based on highly symmetrical, but anisotropic soft-core potentials, such as the Gay–Berne [4]. These have been used to determine the relative importance of steric and dispersive interactions at the various transitions [5]. Work using these generic models is continuing to probe for the essential interactions required for formation of some of the more exotic liquid crystal phases.

Simulation work has also been performed using an atomistic approach, each molecule being represented by a number of bonded atom-based Lennard–Jones interaction sites. A major study of this kind, performed by Wilson and Allen on the molecule CCH5 [6], was able to indicate phase stability at various state points, and yielded information on the variation of the intra- and inter-molecular contributions to the interaction energy in the different phases. That apart, the main focus of such work has been directed at the cyanobiphenyls: a number of different groups have performed molecular dynamics studies of their bulk [7] and adsorption [8] behaviour, using a number of different interaction potentials. Typically, these potentials have incorporated cosine-series torsional potentials for the important dihedral interactions but, despite the degree of electron delocalization within the biphenyl core, have treated each of these torsions independently.

The development and refinement of large-scale electronic structure techniques and fast parallel computer algorithms make it possible to take molecular level calculations substantially further. It is now possible to describe liquid crystal molecules purely from a quantum mechanical perspective. This type of modelling leads to highly accurate structural information [9] and conformational energetics.

In this paper we implement such calculations in the form of density functional theory with a plane wave

*Author for correspondence.

basis set in order to explore the molecular flexibility of the prototype nematogen 5CB. The calculation is performed entirely from first principles where no experimental measurements are used. There are many advantages to this accurate theoretical method, such as the prospect of modelling as-yet unsynthesized molecules.

Here, we apply our *ab initio* method to 5CB where we explore the energetics of twisting the phenyl rings with respect to the position of the pentyl tail, with a view to parameterizing a potential for use in *realistic* empirical computer simulation. There have been recent advances in NMR spectroscopy of liquid crystal fragments where potential functions have been fitted to the relative angle of phenyl rings [10]. We use our method to calculate similar potentials which also give us a measure of the extent to which the separate fragments of the LC molecules interact in different conformations.

The paper is organized as follows: firstly we give a brief description of our technique (a more complete description and a test for accuracy has been given earlier [9]). We then present our results and conclude.

2. Methodology

The method we use for the calculations proceeds as follows: we choose an initial starting configuration for the molecule (in this case we use measurements from benzene and pentane to give an initial structure). We place the molecule in a periodically repeating unit cell surrounded by enough vacuum so that neighbouring molecules are isolated (on testing various vacuum distances we find that a minimum distance of 5 Å is necessary to isolate the molecule in all directions). The valence electronic wave functions are expanded in a plane wave basis set up to an energy cut-off of 700 eV which converges total energy differences to better than 0·001 eV per atom. The core electrons are described via the pseudo-potential approximation. We use the Kleinman–Bylander form [11] for the non-local pseudo-potentials which are generated by the Q_c tuning method of Lin *et al.* [12]. Brillouin zone (BZ) integration is performed by sampling at the gamma point only. Finer BZ sampling is unnecessary since the molecule is isolated, which leads to dispersionless bands. The generalized gradient approximation (GGA) [13] to exchange and correlation, which is shown generally to improve structural details of molecular systems over the local density approximation (LDA), is also used. The total energy of the electronic system is minimized using a preconditioned conjugate gradients scheme. Forces on the atoms are calculated using the Hellmann–Feynman theorem and are then used to calculate the relaxed molecular structure [9, 14].

3. The conformations of 5CB, 0CB and biphenyl
3.1. *Total energy calculations*

We now use the structure calculated [9] using our *ab initio* techniques as the starting point to investigate the conformations of the molecule. The molecule is treated as having three rigid components: the CN–phenyl group, the central phenyl group and the pentyl tail, each having the bond lengths and angles of the relaxed structure as shown in figure 1. We then rigidly rotate each phenyl group about the *para*-axis. The angles of rotation are measured relative to the 'flat' molecule (as illustrated in figure 1). The phenyl rings are stepped by 10° angles through 0°→180° which can be periodically repeated up to 360° by the 2-fold planar symmetry of the rigid body units. In these calculations we consider only the all-*trans*-tail conformation which is known to be, by far, the most highly populated conformation [15]. It is likely that the quantitative degree of influence on the torsional angles will depend slightly on the tail conformation. A detailed survey of these conformational energetics, which in itself is a substantial undertaking for this level of calculation, will appear in a future publication. We calculate the total energy of each of these conformations to build up a 2-dimensional energy landscape. In figure 2 (*a*) we show the energy landscape labelled by the relative angle of the phenyl rings (Θ_r) against the angle of the tail (Θ_t). The lowest energy conformation of the molecule occurs when $\Theta_r = 31°$, with the tail at $\Theta_t = 90°$. This is in excellent agreement with recent X-ray diffraction results [16] on crystalline 5CB at 253 K which indicates that $\Theta_r = 26·3(3)°$ and $\Theta_t = 90·5(3)°$. Note, however, that this X-ray diffraction result relates to low temperature in the solid crystalline form as opposed to these calculations which are for an isolated 5CB molecule and therefore exact agreement would be unexpected.

We have tested our assumption that the conformers remain rigid throughout by allowing a full atomic relaxation for several torsional angles. We find that the energy barriers at 0° and 90° are affected by less than 0·5 kJ mol^{-1}. This is in qualitative agreement with a recent *ab initio* calculation on biphenyl [17] where barrier heights for structural relaxation effects are found to be less that 0·2 kJ mol^{-1}.

We find that the conformational energy of 5CB is most sensitive to the relative angle of the phenyl rings. A large energy barrier exists to the free rotation of the phenyl rings at 90°/270° of approximately 24·1 kJ mol^{-1}. However, the equilibrium structure at $\Theta_r = 31°$ and $\Theta_t = 90°$ is a rather shallow minimum especially in the direction of the tail position (i.e. a line of constant Θ_r, indicating that the pentyl group is relatively free to vibrate around this minimum. The height of the potential barrier to tail rotation (at the optimum relative angle of the rings) is 5·8 kJ mol^{-1} which occurs at 0°/180°,
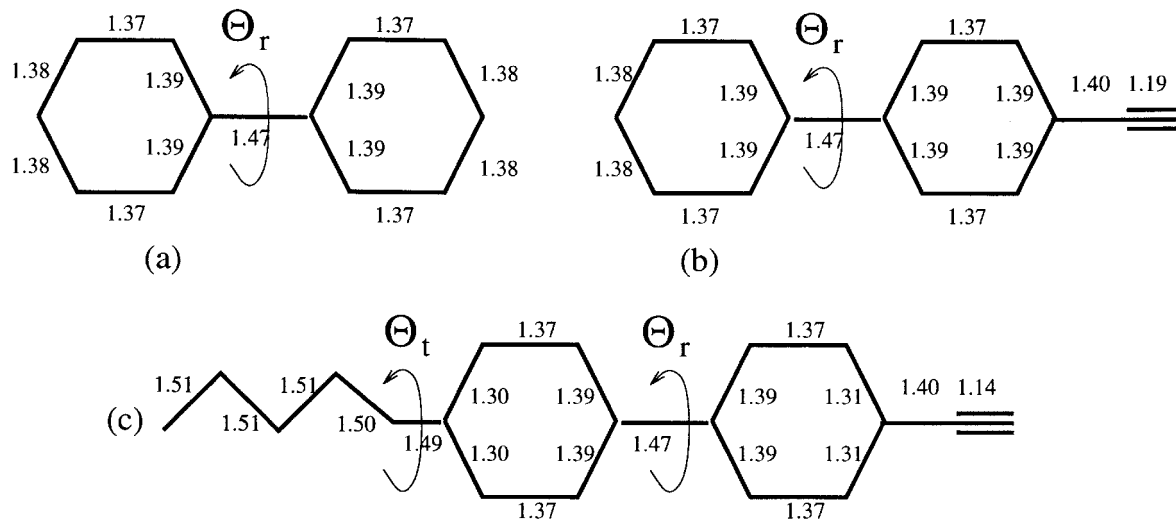
Figure 1. Schematic diagrams of the 5CB molecule and the mesogenic fragments 0CB and biphenyl are shown indicating the rigid units taken in the calculation and defining the angles of rotation. Θ_r is the relative angle between the phenyl rings and Θ_t gives the position at which the tail is lying around the cone in which it rotates. The angle of the apex of the cone is held fixed during the calculations. Both Θ_r and Θ_t are measured relative to the 'flat' molecule.

indicating that the flat molecule is actually an unstable equilibrium position.

Motivated by the difficulty in obtaining an accurate torsional potential for 5CB we now consider mesogen fragments. Recent NMR work by Emsley *et al.* [10] on the molecule cyanobiphenyl (0CB) suggests a potential function for the relative rotation of the phenyl rings derived from nuclear magnetic dipolar couplings of the molecule. In figure 3 we plot the torsional potentials for 0CB and biphenyl mesogen fragments as obtained using our *ab initio* technique, a correlation corrected Hartree–Fock method and the experimental results of Emsley (for 0CB only).

It is found from our calculations that the optimum Θ_r is 38° and 34° for biphenyl and 0CB, respectively. The addition of the CN group is therefore seen to reduce Θ_r, slightly 'flattening' the molecule and also changing the potential barrier heights at 0° and 90°. Our results differ qualitatively from those obtained by the HF technique which predict easier rotation through the 90° configuration and severely hindered rotation through the flat conformer. However our results are in closer agreement with the experimental 0CB results, specifically, the equilibrium torsional angle is far better described by our method, as are the relative barrier heights. The relaxed conformation also differs slightly from other *ab initio* calculations such as those of Rubio *et al.* [17] on biphenyl, where the optimum dihedral angle is given in the range of 38·6° to 46·2° depending on basis set and level of correlation. However, torsional potentials depend sensitively on the basis set, since the deformations are likely to modify bonding, which can

be seen from the range of relaxed torsional angles found in that work, where the angle changes non-monotonically with increasing sophistication of basis set. Our choice of a plane wave basis set completely eliminates such problems, since it is unbiased towards any form of bonding.

3.2. *Probability of 5CB conformers*

A more physical insight into the Θ_r/Θ_t energy plot of 5CB can be gained by recasting the energy scale as a probability density. This is done firstly by calculating the statistical partition function [20]

$$Z = \iint d\Theta_r d\Theta_t \exp[-E(\Theta_r, \Theta_t)/k_B T] \quad (1)$$

which is the normalisation constant for the probability density given by

$$P(\Theta_r, \Theta_t) = \frac{\exp[-E(\Theta_r, \Theta_t)/k_B T]}{Z} \quad (2)$$

where k_B is the Boltzmann constant, T is the given temperature and $P(\Theta_r, \Theta_t)$ is the probability of finding the molecule in the conformational range $(\Theta_r, \Theta_t) \rightarrow (\Theta_r + d\Theta_r, \Theta_t + d\Theta_t)$. A plot of the probability density is shown in figure 2(b). It can now be seen that, although the tail is not completely free to rotate, it will undergo vibrations having a large amplitude with the possibility of rotating through the Θ_t positions of 0°/180° with probability 0·1 brought on by local temperature fluctuations. Conversely, the relative angle of the rings is more rigidly held, with a much deeper potential, with
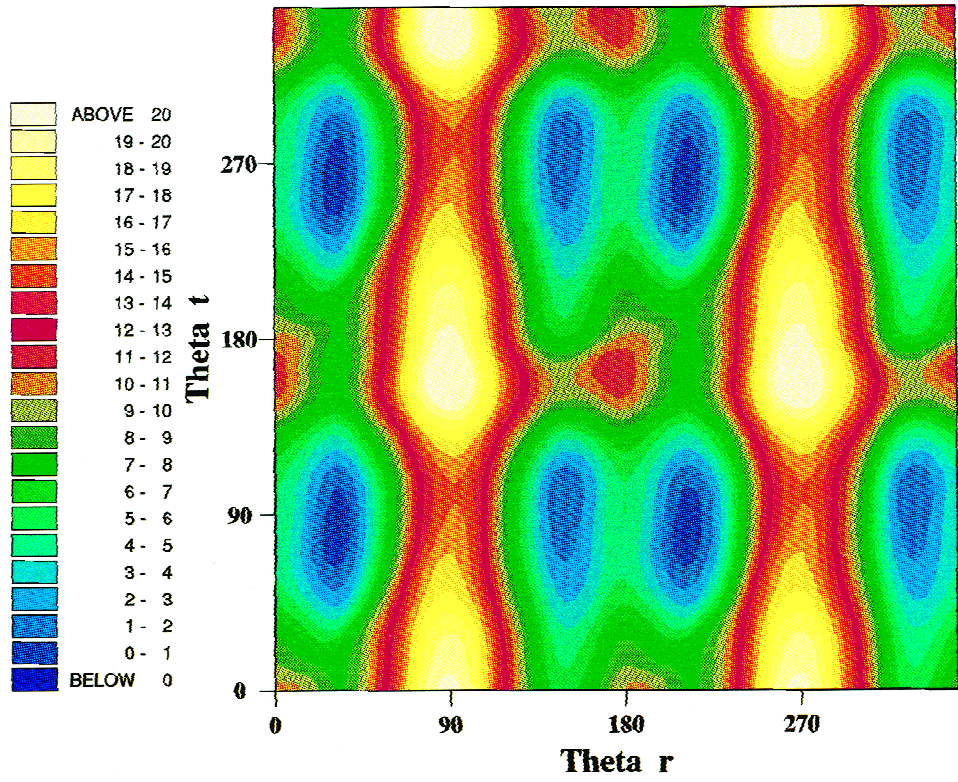
(*a*)
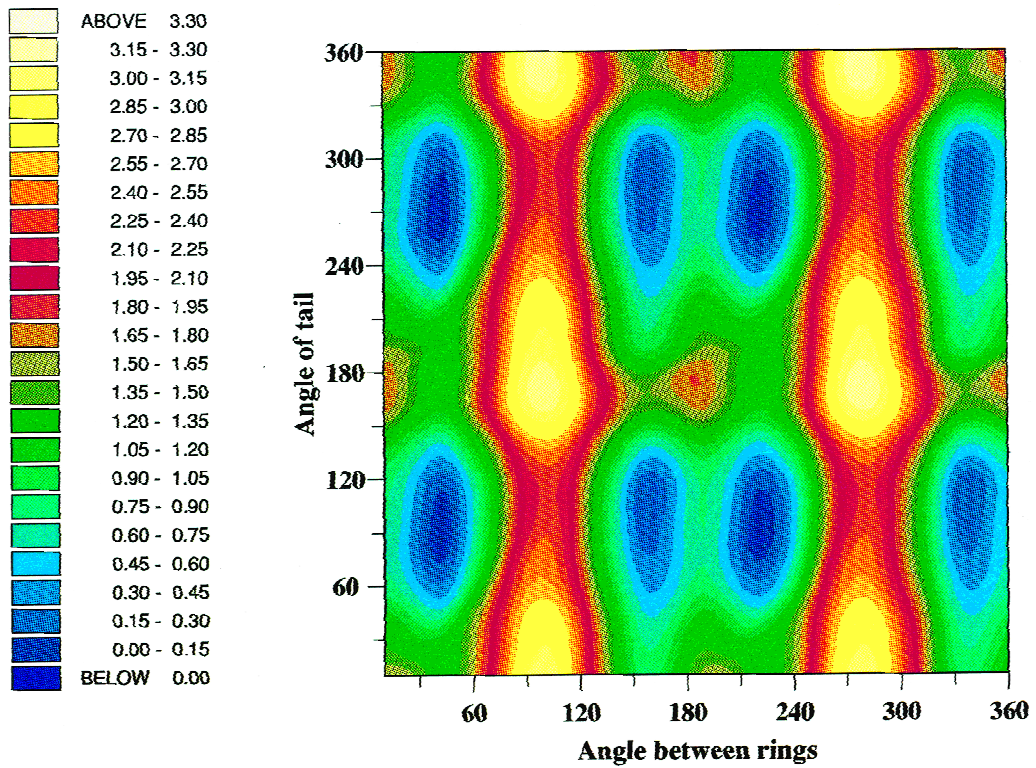
(*b*)

Figure 3. In this diagram we compare our potential functions for 0CB and biphenyl with a recent one calculated from NMR spectra on 0CB by Emsley *et al.* The plot shows the energy as a function of relative phenyl ring angle (Θ_r). The addition of the CN group has some influence on the Θ_r dependence, the relative heights of the energy barriers at 0° and 90° changing significantly. We also compare our conformational potential for biphenyl and OCB with those obtained using the localized 6-31G basis set [18,19], indicated by (*).
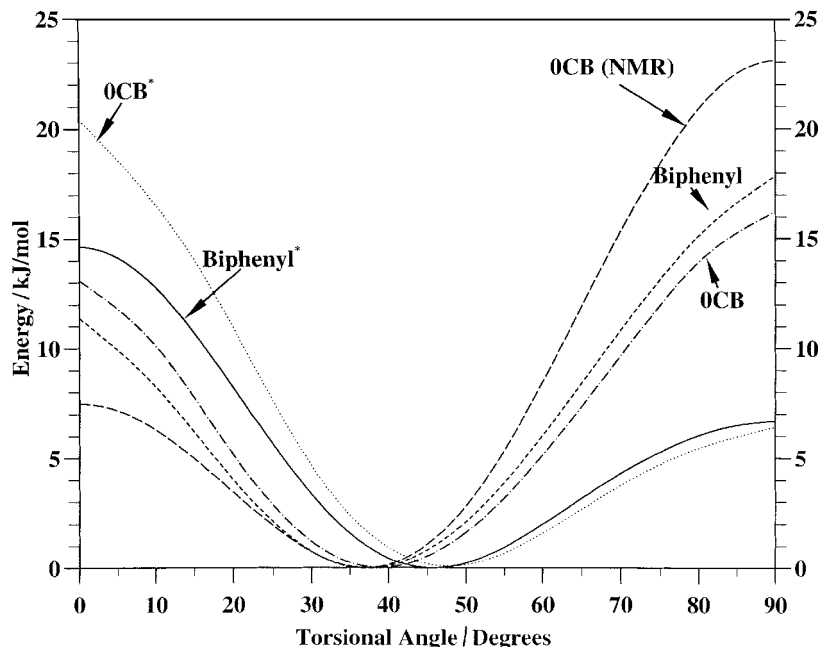
the likelihood of the rings flipping being of the order 0·001.

4. Fitting a potential function

In order for this potential surface to be implemented in realistic empirical calculations, a parameterized function has been fitted. The total energy for each point (Θ_r, Θ_t) has been calculated on a grid discretized by 10° steps. The function is also periodic in both angles and smoothly varying, therefore a natural way to parameterize the potential surface would be to fit Fourier coefficients. This is a relatively straightforward process: the potential is Fourier transformed and the terms which are insignificant are discarded. The potential then takes the form of an inverse Fourier transform

$$E(\Theta_r, \Theta_t) = \sum_{k,l \in \{S\}} a_{kl} \exp\left[-\frac{2\pi i}{360}\left(\frac{l\Theta_r}{36} + \frac{k\Theta_t}{36}\right)\right] \quad (3)$$

except that the sum is over the small set, $\{S\}$, of potential parameters, a_{kl}, given in table 1. The factor of 36 in the above equation indicates the 'granularity' used in the *ab initio* calculations, i.e. 36 angles were used in the range $0° \rightarrow 360°$.

This form of the potential is simple to use in molecular dynamics simulations since analytic derivatives for forces

and molecular vibrations are easily calculated. Depending on the circumstances, the potential can be evaluated with 10 exponentials. This represents a comparable computational expense to the alternative calculation of two- (i.e. one for each dihedral angle) four- or five-term cosine series.

We also fit the 1d potentials for biphenyl and 0CB in a similar form to that of Emsley *et al.* [10], by taking the important cosine terms in a Fourier series thus:

$$V(\Theta_r) = \sum_{n \in \{S\}} c_n \cos\left(\frac{2\pi n\Theta_r}{360}\right), \quad (4)$$

Table 1. Coefficients of the potential.

Potential parameters	Coefficient
$a_{0,0}$	$9\cdot2760 + 0\cdot0000i$
$a_{0,2} = a^*_{0,34}$	$1\cdot6622 - 0\cdot4605i$
$a_{0,4} = a^*_{0,32}$	$-0\cdot0704 - 0\cdot3556i$
$a_{0,6} = a^*_{0,30}$	$-0\cdot2513 - 0\cdot0311i$
$a_{2,0} = a^*_{34,0}$	$-2\cdot9485 - 0\cdot0647i$
$a_{2,32} = a^*_{34,4}$	$0\cdot2169 + 0\cdot0466i$
$a_{2,34} = a^*_{34,2}$	$0\cdot1666 + 0\cdot2258i$
$a_{4,0} = a^*_{32,0}$	$1\cdot8287 - 0\cdot0381i$
$a_{4,32} = a^*_{32,4}$	$0\cdot1803 + 0\cdot0657i$
$a_{0,6} = a^*_{30,0}$	$0\cdot3344 - 0\cdot0106i$

Figure 2. Conformational energy landscape of the 5CB molecule is shown in (*a*) where the units are in kJ mol^{-1}. In this plot the total energy for all angles between the phenyl rings (Θ_r) against the angle of the pentane tail (Θ_t) is given. As a measure of the likelihood of finding any given conformation of the molecule at room temperature (300 K) we show in (*b*) the probability density. The units are in a logarithmic scale and measured relative to the most likely conformation (which has been given a probability density of $1 = 10°$). For example, a probability density of x on this scale means that given conformation is 10^{-x} less likely to be found than the ground state.

Table 2.   Coefficients c_n for biphenyl and OCB.

i	c_n for biphenyl	c_n for OCB
0	6·84858	6·89641
2	− 2·43155	− 4·00950
4	6·94367	6·74595
6	0·81483	0·74868
8	0·71154	0·71462
10	0·02516	0·02354
12	0·09522	0·08927

where $\{S\}$ is the set of indices to be summed over. The values of the coefficients, c_n, are given in table 2.

5.   Discussion

It is only now possible with recent advances in computer speed to perform first principles electronic structure calculations on molecules which form liquid crystalline phases. We have been able accurately to map out accurately the energy surface of the 5CB molecule over two rotational angles. We find, contrary to the assumptions of earlier work, that the alkyl chain does have a significant effect on the relative angle between the rings, in that the energy barriers between similar low energy configurations are changed. As 'minor' differences like this in molecular shape give drastic effects on the macroscopic phase behaviour, accurate modelling of this type is necessary to understand fully the complex behaviour of liquid crystal phases.

References

[1] LEBWOHL, P. A., and LASHER, G., 1972, *Phys. Rev. A*, **6,** 426; ZHANG, Z., MOURITSEN, O. G., and ZUCKERMAN, M. J., 1992, *Phys. Rev. Lett*., **69,** 2803.

[2] FRENKEL, D., 1987, *Mol. Phys*., **60,** 1; ALLEN, M. P., EVANS, G. T., FRENKEL, D., and MULDER, B. M., 1993, *Adv. chem. Phys*., **86,** 1.

[3] HANSEN, J. P., and MCDONALD, I. R., 1986, *Theory of Simple Liquids*, 2nd Edn. (New York: Academic Press).

[4] GAY, J. G., and BERNE, B. J., 1981, *J. chem. Phys*., **74,** 3316; RULL, L. F., 1995, *Physica A*, **220,** 113.

[5] LUCKHURST, G. R., and SYMMONDS, P. S. J., 1993, *Mol. Phys*., **80,** 223.

[6] WILSON, M. R., and ALLEN, M. P., 1992, *Liq. Cryst*., **12,** 157.

[7] KOMOLKIN, A. V., MOLCHANOV, YU. V., and YAKUTSENI, P. P., 1989, *Liq. Cryst*., **6,** 39; PICKEN, S. J., VAN GUNSTEREN, W. F., VAN DUIJNEN, P. TH., and DE JEU, W. H., 1989, *ibid*, **6,** 357; CROSS, C. W., and FUNG, B. M., 1994, *J. chem. Phys*., **101,** 6839.

[8] YONEYA, M., and IWAKABE, Y., 1995, *Liq. Cryst*., **18,** 45; CLEAVER, D. J., CALLAWAY, M. J., FORESTER, T., SMITH, W., and TILDESLEY, D. J., 1995, *Mol. Phys*., **86,** 613.

[9] CLARK, S. J., ADAM, C. J., WHITE, J., ACKLAND, G. J., and CRAIN, J., 1997, *Liq. Cryst*., this issue.

[10] EMSLEY, J. W., HORNE, T. J., CELEBRE, G., DELUCA, G., and LONGERI, M., 1992, *J. chem. Soc. Faraday Trans*., **88,** 1679.

[11] KLEINMAN, L., and BYLANDER, D. M., 1982, *Phys. Rev. Lett*., **48,** 1425.

[12] LIN, J. S., QTIESH, A., PAYNE, M. C., and HEINNE, V., 1993, *Phys. Rev. B*, **47,** 4147.

[13] PERDEW, J. P., and WANG, Y., 1992, *Phys. Rev. B*, **45,** 13244.

[14] PAYNE, M. C., TETER, M. P., ALLEN, D. C., and JOANOPOULOS, J. P., 1992, *Rev. mod. Phys*., **64,** 1045.

[15] WILSON, M., 1996, *Liq. Cryst*., **21,** 437.

[16] HANEMANN, T., HAASE, W., SVOBODA, I., and FEUSS, H., 1995, *Liq. Cryst*., **19,** 669.

[17] RUBIO, M., MERCHAN, M., and ORTI, E., 1995, *Theor. Chim. Acta*, **91,** 17.

[18] TSUZUKI, S., and TANABE, K., 1991, *J. phys. Chem*., **95,** 139.

[19] CLEAVER, D. J., and TILDESLEY, D. J., 1994, *Mol. Phys*., **81,** 781.

[20] MANDEL, F., 1988, *Statistical Physics* (J. Wiley & Sons).