Monte Carlo simulation of discotic Gay–Berne mesogens with axial dipole

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We have studied a system of $N = 10^3$ discotic particles with a central axial dipole using Monte Carlo computer simulations. We have investigated four temperatures corresponding to isotropic, nematic and columnar liquid-crystal phases determining the molecular and dipolar distributions and the length of the polar domains in the columns.

Discotics form a rapidly growing family of liquid crystals. The typical structure of a discotic is that of a flat core with a certain number of chains attached.[1] The central core has been realized with a large variety of aromatic structures, starting in particular from the classic triphenylene and truxene ones, to include now superyines and a large variety of other moieties.[2,3] An interesting possibility is that offered by metalloorganic compounds, where a suitable transition metal helps in organizing a set of ligands with an appropriate planar geometry.[4] This increasing freedom and flexibility in the choice of structures allows the possibility of selecting cores and inserting groups, that confer to the molecular properties of interest in view of applications, such as charge-transfer ability or a suitable electrostatic moment. Here we study a simple case of this kind, that of discs with an axial permanent dipole in the centre, to determine their overall molecular and dipolar organization. Structures resembling this exist in organometallic complexes[5,6] and, to some extent, in certain organic mesogens.[7] In particular, polar discotic metallomesogens based on vanadyl 1,3-diketonate complexes[5,6] have a large dipole moment normal to the plane of the molecule and have been found to give columnar phases.

Despite the growing importance of discotic systems, the number of computer simulations has been relatively small. Discotic systems have been modelled with hard-cut spheres[8,9] and hard-cut spheres with axial dipoles[10] and with circular patches of dipoles[11] have also been studied. This last system shows ferroelectric behaviour, at least in the case of columns with complete orientational order and of conducting boundary conditions. In contrast, antiferroelectric ordering of the dipoles in the column was observed for point axial dipoles.[10] Notice, however, that in these hard-core systems, the only temperature dependence comes from the dipolar energy part, making it difficult to perform reasonable comparisons with thermotropic systems.

Here we shall model the discotic mesogen using a Gay–Berne[12] attractive–repulsive potential that has already proved capable of yielding discotic nematic and columnar phases.[13,14] We shall then employ Monte Carlo (MC) simulations to obtain the resulting equilibrium molecular organization at a few selected temperatures. Model and simulation details are given in the next section, while in the following ones we present our results and conclusions.

The model and its simulation

We consider a system of uniaxial oblate ellipsoidal particles of axes σ_e and σ_s, with $\sigma_e < \sigma_s$ and with an embedded electric dipole. The pair potential is the sum of a Gay–Berne (GB)[12,15] and a dipole–dipole (dd) term: $U_{ij}^* = U_{GB}^* + U_{dd}^*$. The GB term has a repulsive and attractive contribution with a 12–6 inverse distance dependence form:

$$U_{GB}^*(\hat{u}_i, \hat{u}_j, r) = 4\varepsilon_s \, \varepsilon(\hat{u}_i, \hat{u}_j, \hat{r})$$
$$\times \left[\left\{ \frac{\sigma_e}{r - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}) + \sigma_e} \right\}^{12} \right.$$
$$\left. - \left\{ \frac{\sigma_e}{r - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}) + \sigma_e} \right\}^6 \right] \quad (1)$$

with unit vectors $\hat{u}_i, \hat{u}_j$ defining the orientation of the axis of particles i and j; $r = r_j - r_i \equiv r\hat{r}$ the intermolecular vector of length r. The rather complicated anisotropic contact distance $\sigma(\hat{u}_i, \hat{u}_j, \hat{r})$ and interaction energy $\varepsilon(\hat{u}_i, \hat{u}_j, \hat{r})$ are defined as in ref. 12. We employ a parametrization related to that used by Emerson et al. in ref. 13 and originally based on the dimensions of a triphenylene core, namely, shape anisotropy $\sigma_e/\sigma_s = 0.345$, interaction anisotropy $\varepsilon_e/\varepsilon_s = 5$, but using, instead, energy parameters $\mu = 1$ and $v = 3$ as in ref. 15. σ_s and ε_s are used as molecular units of length and energy. The cut-off radius adopted is $r_c = 1.4\sigma_s$. We show elsewhere that this discotic GB system gives anisotropic, discotic nematic and hexagonal columnar phases.[16] The dipolar energy is given by

$$U_{dd}^* = \frac{\mu_i^* \mu_i^*}{r^3} [\hat{u}_i \cdot \hat{u}_j - 3(\hat{u}_i \cdot \hat{r})(\hat{u}_j \cdot \hat{r})] \quad (2)$$

where we consider axial dipole moments $\mu_i^* \equiv \mu^* \hat{u}_i$, $\mu_j^* \equiv \mu^* \hat{u}_j$ [the dimensionless $\mu^* \equiv (\mu^2/\varepsilon_s \sigma_s^3)^{1/2}$] positioned in the centre of the molecule. We have used a reduced dipole moment $\mu^* = 0.8$ which, when considering, for instance, a molecular diameter of $\sigma_s = 9.27$ Å, and an energy term $\varepsilon_s = 0.49 \times 10^{-14}$ erg, corresponds to ca. 1.6 D.

We have performed extensive canonical ensemble (constant number of molecules N, volume V and temperature T) Monte Carlo simulations of a system of $N = 1000$ interacting particles enclosed in a cubic box with periodic boundary conditions at a reduced density $\rho^* \equiv N\sigma_s^3/V = 2.5$. We have concentrated on four dimensionless temperatures $T^* \equiv kT/\varepsilon_s = 20.0, 10.0, 7.0$ and 2.0 that belong to isotropic (I), nematic (N) and columnar phases (C) with different degrees of alignment. At these temperatures, the reference state in the absence of dipoles[16] shows an isotropic phase, a low-ordered nematic close to the N–I transition, a nematic and a columnar phase. In Fig. 1 we report the temperature dependence of the second-rank order parameter $\langle P_2 \rangle$ for the reference apolar system (continuous curve) and that with dipoles (points). The MC runs were started from well equilibrated configurations of the dipoleless system, even though at the lowest temperature
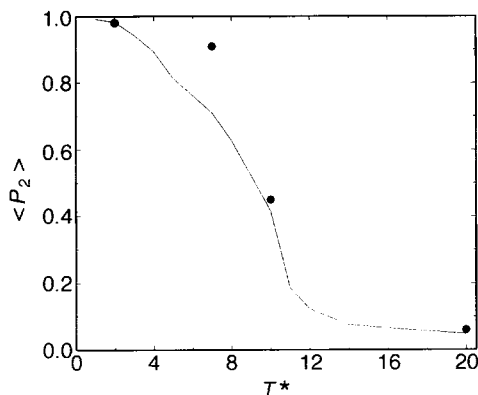
Fig. 1 Average orientational order parameter $\langle P_2 \rangle$ for the system of dipolar discs as a function of temperature (●). The behaviour of the dipole-less system, here used as reference state, is reported as a continuous line.

some hole development was observed.[14,16] A preliminary randomization of the dipole orientation (sign of the molecular z-axis) was necessary to start from a non-ferroelectric phase ($\langle P_1 \rangle = 0$). Each sample was then equilibrated from a minimum of 50 kcycles to a maximum of 350 kcycles, where a cycle corresponds to N attempted moves. The production runs were from 50 to 200 kcycles long. In order to speed up the equilibration process, we have also found it essential to allow the dipoles to flip head to tail. In practice, flip moves are attempted with a probability of 0.05.

The long-range dipolar potential contributions were evaluated using the Ewald sum technique[17] with tin foil boundary conditions (relative permittivity $\varepsilon_1 = \infty$ outside the simulation box, which is the standard choice in this type of calculation) and employing the same parameters as used in ref. 18. This is a very reliable but time-consuming method and the calculations were run using parallel computing techniques[18] on a cluster of workstations using PVM.[19] Another version of the code, with a replicated data structure where each of the processors calculates the energy contribution of a subset of particles, was run on a Cray T3D with 128 processors.

Results and Discussion

In Table 1 we report the most important thermodynamic observables for the temperatures studied. Here $\langle P_2 \rangle$ is calculated from the largest eigenvalue of the ordering matrix[20] and, using the associate eigenvector d as phase director, we compute the first rank order parameter as $\langle P_1 \rangle = \langle \hat{u}_i \cdot d \rangle_i$. We report also the scalar dielectric constant $\bar{\varepsilon} = 1 + 4\pi\rho^*[\langle M \cdot M \rangle - \langle M \rangle \cdot \langle M \rangle]/(3NT^*)$, where $M = \sum_{i=1}^{N} \mu_i^*$ is the total dipole moment. We notice that the columnar phase at $T^* = 7.0$ is apparently slightly ferroelectric ($\langle P_1 \rangle \approx 0.14$), even though our samples are probably not large enough to establish this unambiguously, and further investigation is under way.

Table 1 Results from MC simulation of $N = 1000$ systems of GB disc-like molecules with central dipole μ^* parallel to the molecular z axis

T^*	phase	$\langle U^* \rangle$	$\langle P_2 \rangle$	$\langle P_1 \rangle$	$\bar{\varepsilon}$
2.0	C	-54.4 ± 0.2	0.98 ± 0.01	0.03 ± 0.03	1.1 ± 0.1
7.0	C	-40.1 ± 0.4	0.91 ± 0.01	0.14 ± 0.01	1.2 ± 0.1
10.0	N	-16.0 ± 0.6	0.45 ± 0.05	0.03 ± 0.02	1.9 ± 0.2
20.0	I	-1.0 ± 0.6	0.06 ± 0.02	0.00	1.5 ± 0.1

We report the reduced energy $\langle U^* \rangle$, the order parameters $\langle P_2 \rangle$, $\langle P_1 \rangle$ and the relative permittivity constant $\bar{\varepsilon}^{17}$ at four reduced temperatures T^* corresponding to the phases indicated.

We now describe the structures adopted by the sample at the different temperatures shown in the snapshots in Plate 1. We examine, first, the distribution of particle centres as a function of the molecular separation r, as shown by the radial correlation function $g_0(r) = 1/(4\pi r^2 \rho)\langle \delta(r - r_i) \rangle_{r_i}$ and its anisotropies. The $g_0(r)$ for the low-temperature columnar phase ($T^* = 2.0$), shown in Fig. 2 presents several well defined peaks related to the detailed structure of this mesophase. The first two maxima correspond to the first two neighbouring pairs within the same column (face-to-face). The next two maxima are due to adjacent pairs of molecules belonging to different columns (side-by-side) and their position ($r/\sigma_s \approx 0.9$ and $r/\sigma_s \approx 1.1$) is typical of a hexagonal arrangement of inter-digitated columns, also found in the apolar system.[16] Notice, however, that at higher distances r, the position of the peaks corresponds to molecules belonging either to the same or to different columns and a simple assignment can be misleading. Similar features are found in $g_0(r)$ for the $T^* = 7.0$ sample, albeit less structured. In particular, the two intracolumn peaks are less sharply defined and the fingerprint of the hexagonal ordering is not fully resolved. This broad peak shows a hump at $r/\sigma_s > 1$. At this temperature the columns are still arranged in a hexagonal fashion but without inter-digitation. A further increase in temperature ($T^* = 10.0$) gives a nematic phase and the radial correlation function for the nematic phase shows no positional ordering: side-by-side configurations are approximately as probable as face-to-face.

Further details on phase structure can be found by studying the second-rank anisotropy $g_2^+(r) = \langle P_2(\cos \beta_{r_i}) \rangle_{r_i}$, where β_{r_i} is the angle between the intermolecular vector and the phase director[15] (Fig. 3). For the columnar phases the anisotropy exhibits a detailed structure, even for high molecular separations. For these temperatures ($T^* = 2.0, 7.0$) the columns are well defined and they extend across the whole MC sample. A close look at the curves shows two positive maxima for the intracolumn neighbouring pairs (intermolecular vector parallel to the director) and a third negative peak corresponding to side-by-side molecules belonging to adjacent columns (intermolecular vector perpendicular to the director). For the two lowest temperatures the average length of the columns is roughly seven molecules (Table 2), where we operationally define a column as a cluster formed by at least three adjacent face-to-face molecules. We have also determined the length of polar domains, i.e., portions of columns with dipoles parallel to each other. At temperature $T^* = 2.0$ the average polar domain length is 6, while at $T^* = 7.0$ it is 5 (Table 2). At the latter temperature there is a slight imbalance (25%) in the populations of up and down domains, at least three times higher than that at other temperatures. Since each domain is formed by a considerable number of molecules and the size of the sample is finite we find a non-zero first-rank order parameter and the columnar phase at $T^* = 7.0$ appears to be weakly ferroelectric. It is possible that this effect might disappear using bigger samples. Notice that a ferroelectric system would

Table 2 Average length ($\langle l_{col} \rangle$) and number ($\langle n_{col} \rangle$) of 'columns' at the four temperatures studied

| T^*	$\langle l_{col} \rangle$	$\langle n_{col} \rangle$	$\langle l_{up} \rangle$	$\langle n_{up} \rangle$	$\langle l_{dn} \rangle$	$\langle n_{dn} \rangle$
2.0	7.3	129	5.9	86	5.9	81
7.0	6.5	127	5.1	101	5.3	74
10.0	3.4	42	2.3	80	2.3	89
20.0	3.1	96	1.7	97	1.7	99

The average lengths ($\langle l_{up} \rangle$, $\langle l_{dn} \rangle$) and numbers ($\langle n_{up} \rangle$, $\langle n_{dn} \rangle$) of dipolar domains pointing up and down with respect to the phase director are also reported. We define as 'columns' sequences of three or more adjacent molecules (i.e. face-to-face). For molecules within the same column we define 'domains' as sequences of two or more parallel dipoles (i.e. up or down).
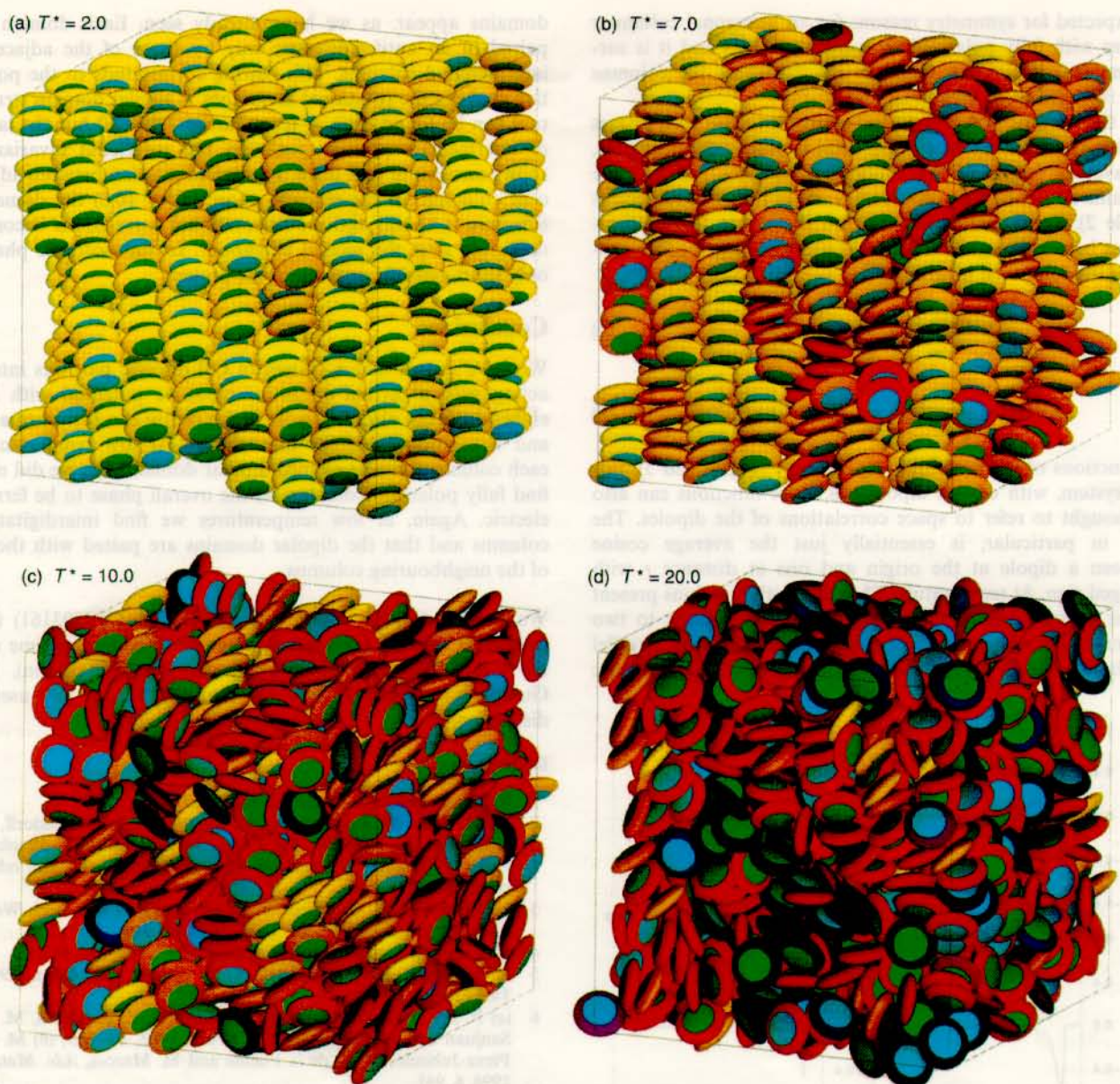
Plate 1 Snapshots of configurations for systems at $T^* = 2.0$ (a), 7.0 (b), 10.0 (c) and 20.0 (d). Molecular orientation with respect to the director is rendered using a colour map ranging from yellow (parallel) to blue (perpendicular). The green and cyan 'patches' are used to distinguish head from tail of molecular dipoles.
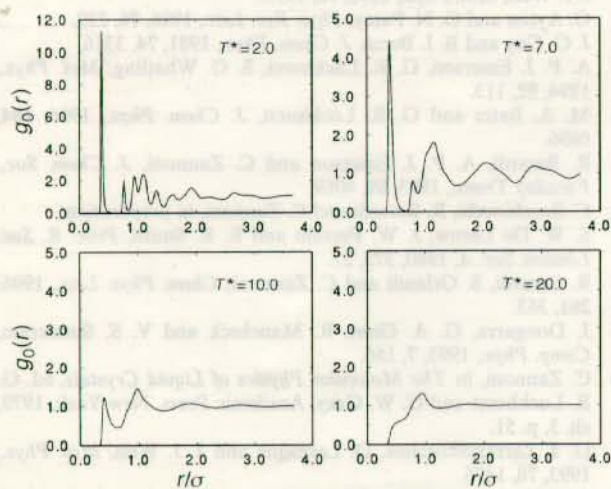
Fig. 2 Radial correlation function $g_0(r)$ for the system of dipolar discs at the four temperatures studied
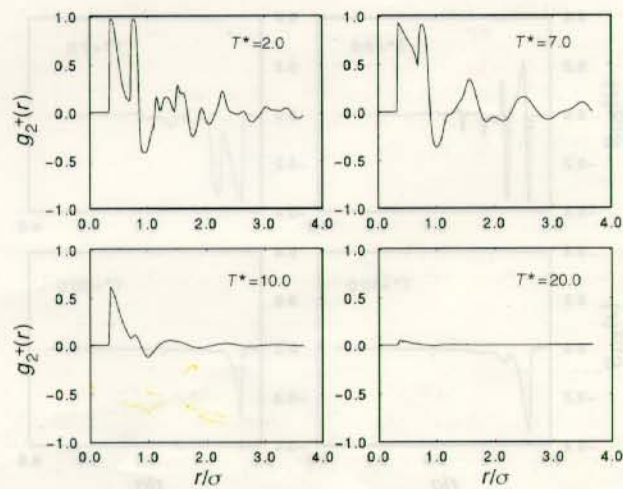
Fig. 3 Second-rank anisotropy of the radial correlation function $g_2^+(r)$ for the system of dipolar discs at the four temperatures studied

be expected for symmetry reasons for an hexagonal columnar system with fully polarized individual columns and it is surprising that it was not found in ref. 21, where the columns were reported to be fully polarized.

In the nematic ($T^* = 10.0$) and isotropic ($T^* = 20.0$) phases the face-to-face clustering of particles is practically negligible, the average length of the columns is roughly 3–4 and the domains do not contain, on average, more than two molecules (Table 2). Some further insight into the orientational correlations between neighbouring molecules can be gained by analysing the rotational invariants[22]

$$S^{110}(r) = -\frac{1}{\sqrt{3}} \langle u_i \cdot u_j \rangle_{ij} \quad (3)$$

and

$$S^{112}(r) = \frac{1}{\sqrt{30}} \langle u_i \cdot u_j - 3(u_i \cdot \hat{r})(u_j \cdot \hat{r}) \rangle_{ij} \quad (4)$$

as functions of the molecular separation r (Fig. 4 and 5). For this system, with central dipole $\mu \| u$, these functions can also be thought to refer to space correlations of the dipoles. The first, in particular, is essentially just the average cosine between a dipole at the origin and one at distance r with changed sign. At temperature $T^* = 2.0$, both functions present a pair of well defined negative peaks corresponding to two orders of intracolumn neighbouring molecules with parallel dipolar moments. Within each column, small ferroelectric

Fig. 4 Orientational correlation function $S^{110}(r)$ for the system of dipolar discs at the four temperatures studied

Fig. 5 Orientational correlation function $S^{112}(r)$ for the system of dipolar discs at the four temperatures studied

domains appear, as we have already seen. Each domain is paired in an antiferroelectric way by those of the adjacent interdigitated columns. This pairing corresponds to the positive peaks in the rotational invariants. A similar domain structure can be found even at temperature $T^* = 7.0$ but the lack of intermediate positive peaks in the rotational invariants shows once more that there is no interdigitation between adjacent columns. In the nematic phase ($T^* = 10.0$) the domain structure is absent and the orientational correlations become negligible after the second neighbour. In the isotropic phase only short-ranged correlations are present.

Conclusions

We have shown that a system of GB discotic particles interacting with a certain attractive–repulsive potential with an embedded axial electric dipole in the centre can form nematic and hexagonal columnar mesophases. At low temperature, each column contains aligned dipolar domains but we did not find fully polarized columns, or the overall phase to be ferroelectric. Again, at low temperatures we find interdigitated columns and that the dipolar domains are paired with those of the neighbouring columns.

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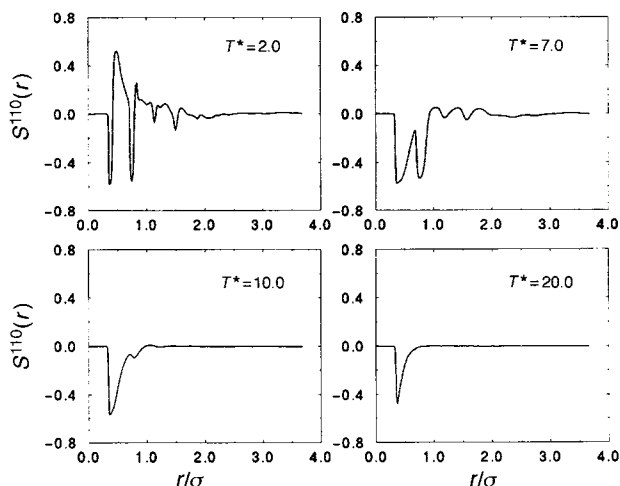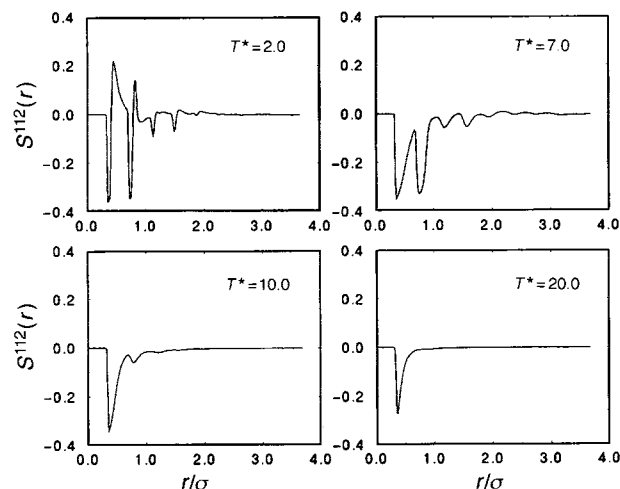22. A. J. Stone, *Mol. Phys.*, 1978, **36**, 241.