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## Chain formation in a model dipolar liquid: computer simulation study

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**Abstract.** We have performed molecular dynamics (MD) simulations along a low-temperature isotherm for a system of strongly dipolar elongated molecules. The model molecules are found to associate to form well defined chains; this association is induced by the dipolar interaction. The order parameters, the polarization and the average number of molecules in a chain have been calculated for a range of densities.

It is only recently that systems of strongly interacting dipolar spheres have been investigated in some detail by means of computer simulations. It has been shown that in the absence of long-range positional order the strong spatial–orientational coupling intrinsic to dipolar forces can lead to interesting new phase behaviour. The molecular dynamics (MD) calculations of Wei and Patey [1–3] for the model of soft spheres with electric point dipoles embedded at their centres represent the first contribution which shows that the dipolar interaction *alone* is capable of bringing about the formation of an orientationally ordered phase. Moreover these authors showed that this phase is a ferroelectric liquid crystal, becoming a stable ferroelectric solid at high density.

The Monte Carlo (MC) simulations of Weis *et al* [4] for a system of strongly interacting dipolar hard spheres have revealed that dipolar hard spheres can also form an orientationally ordered ferroelectric fluid and solid phases. In subsequent papers, Levesque and Weis [5, 6] extended their previous MC calculations to lower densities and temperatures. The most interesting finding was the formation of well defined chains with near contact of the hard spheres and head-to-tail alignment of the dipole moments.

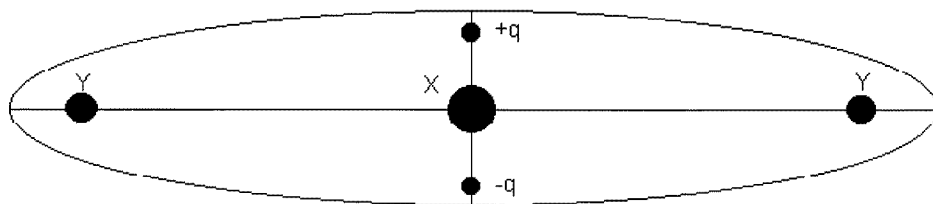
The systems of spheres with point dipoles are highly idealized ones. The question arises of whether these intriguing new phases—induced by the dipolar interaction alone and reported so far only for point dipole spheres (soft or hard)—may also be expected for somewhat less idealized, more complex, intentionally more realistic systems. One would like to consider the very general case of an ensemble of non-spherical particles with a certain distribution  $\{q_k\}$  ( $\sum_k q_k = 0$ ;  $k = 1, 2, \dots$ ) of effective electric charges  $q_k$  spread out over the volume of each particle. The dipole moment of such a particle is determined by a distribution of electric charges (not point dipoles). Moreover, for some distributions of effective charges, higher electric multipoles may appear as well.

In the following we take a preliminary step in this direction. We test the effect of removing three major limiting assumptions appearing in the previous calculations [1–6], i.e. (a) spherical symmetry of the particles, (b) a one-site interaction potential only, and (c) a point dipole moment embedded at the centre of each sphere.

To this end we have performed MD simulations for the simple model which consists of elongated molecules (ellipsoids of revolution) with three embedded interaction sites  $XY_2$  placed on the major axis of the molecule. The sites  $Y-X-Y$  are responsible for the non-dipolar intermolecular interaction of atomic groups (united atoms or pseudoatoms) located inside the molecule. The three-site intermolecular potential generates translatory as well as *rotatory* dynamics of our molecules even in the absence of dipole–dipole interaction. The potential  $U_{ij}$  of a pair of different molecules  $i$  and  $j$  is therefore a sum of two contributions  $U_{ij} = U_{ij}^{SS} + U_{ij}^C$ . The first term  $U_{ij}^{SS}$  is the sum of the assumed site–site soft-sphere potentials  $U_{i\alpha j\beta}$ :

$$U_{i\alpha j\beta}^{SS} = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta}/r_{i\alpha j\beta})^{12} \quad (1)$$

where  $r_{i\alpha j\beta}$  is the distance between the site  $\alpha$  of molecule  $i$  and the site  $\beta$  of molecule  $j$ ,  $\epsilon_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  are the soft-sphere potential parameters, and  $\alpha, \beta = X, Y$ .



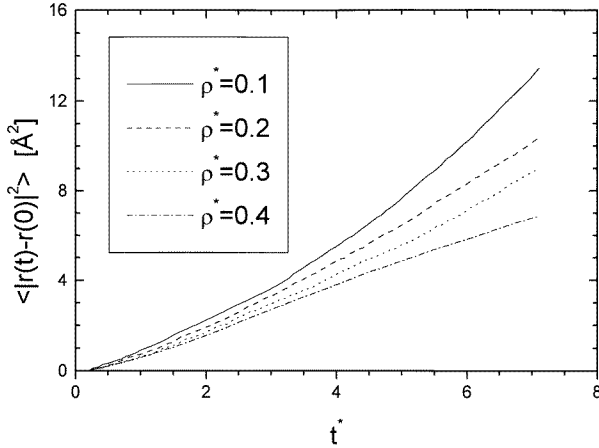
**Figure 1.** A sketch of the molecular model. The relevant labels, explained in the text, are shown.

To date, the only ferroelectric liquid crystals which have been observed are chiral smectic-C phase ones. The presence of polar groups located beside the rod-like central cores, with strong components perpendicular to the central axis, is usual in smectic-phase-forming systems. The model that we are describing is primitive; it is not our aim at this stage to model a fully realistic molecule which could possibly form the ferroelectric liquid crystal phase. Nevertheless, guided by this experimental observation, we equip our elongated molecule with two effective charges  $\{q, -q\}$  located on opposite sides of the central pseudoatom  $X$ , perpendicular to the  $XY_2$  axis and with the distance  $d_q$  between them. In other words, the molecule has the dipole moment  $\mu$  ( $\mu = |\mu| = qd_q$ ) located centrally and perpendicular to the symmetry axis of the molecule (see figure 1).

The second component  $U_{ij}^C$  of the pair potential  $U_{ij}$  is therefore the sum of the Coulomb interactions between the electric charges  $\{q_k\}$  of molecules  $i$  and  $j$ . The total potential energy  $U$  of the sample of  $N$  particles is given by  $U = \sum_{i,j=1}^N (U_{ij}^{LJ} + U_{ij}^C)$  ( $j > i$ ).

Our MD simulations were performed on a canonical  $NVT$ -ensemble ( $V$  and  $T$  are the volume and the absolute temperature of the sample, respectively) of 500 particles in a cubic box with periodic boundary conditions, employing the Gaussian isokinetic equation of motion as described by Kusalik [7]. The orientational coordinates of the particles were expressed in terms of quaternion parameters and the equations of motion were integrated using the Beeman algorithm [8]. The long-range Coulomb interactions were handled using the Ewald summation technique in three dimensions [8] with the standard assumption that the dielectric permittivity  $\epsilon'$  of the surrounding continuum is infinite ( $\epsilon' \rightarrow \infty$ ) [2, 5, 6, 8, 9]. Extensive MD studies of the convergence of the Ewald sum have been carried out by Kusalik [7] and we have followed his method of optimization of Ewald's summation. In the present calculations, we used the real ( $R_c$ ) and reciprocal ( $k_c$ ) cut-off radii  $R_c = L/2$ ,  $k_c = 30.7/L$ , where  $L$  is the length of the cubic simulation cell, and the Ewald sum

parameter  $\alpha^* = 6.4$  (as defined in [7]). Tests with other values of the parameter  $\alpha^*$  were also carried out. We have verified that our results were not sensitive to the particular value chosen for  $\alpha^*$ , unless it is in the range  $5.0 < \alpha^* < 7.0$ . Typically, runs were begun with randomly oriented and fcc-placed particles and were equilibrated for about 50 000 time steps. Averages were then collected for at least another 100 000 time steps. It is convenient to characterize a dipolar fluid by specifying the reduced density  $\rho^* = Nl^3/V = \rho l^3$ , the reduced temperature  $T^* = k_B T l^3 / \mu^2$ , the reduced dipole moment  $\mu^* = \sqrt{l/T^*}$ , the reduced time step  $\Delta t^* = \Delta t / (ml^5 / \mu^2)^{1/2}$ , and the reduced components of the moment of inertia with respect to the major molecular axis  $I_{\parallel}^* = I_{\parallel} / (ml^2)$ ,  $I_{\perp}^* = I_{\perp} / (ml^2)$ , where  $k_B$  is the Boltzmann constant,  $\rho = N/V$  is the number density,  $m$  is the mass of the molecule, and  $l$  is the Y–Y distance. Here the applied values of the model parameters are:  $\Delta t^* = 0.0072$ ,  $\mu^* = 3.5$  ( $\mu = 4$  D),  $I_{\parallel}^* = 0.011$ ,  $I_{\perp}^* = 0.055$ , and  $d_q/l = 0.3$ . The reduced parameters of the soft-sphere potential are:  $\varepsilon_{XX}^* = \varepsilon_{XX} l^3 / \mu^2 = 0.063$ ,  $\varepsilon_{YY}^* = \varepsilon_{YY} l^3 / \mu^2 = 0.013$ , and  $\sigma_{XX}^* = \sigma_{XX} / l = 0.874$ ,  $\sigma_{YY}^* = \sigma_{YY} / l = 0.584$  with the Lorentz–Berthelot mixing rules for the cross (XY) interaction parameters. Simulations were performed along a low-temperature isotherm with  $T^* = 0.0816$  for a range of densities,  $\rho^* = 0.05$ – $0.4$ .



**Figure 2.** The mean square displacement  $\langle |r(t) - r(0)|^2 \rangle$  as a function of the reduced time  $t^*$  for a range of densities  $\rho^*$ .

The possible existence of an ordered phase (nematic, ferroelectric, ...) [10] was monitored by calculating the usual equilibrium first- and second-rank orientational order parameters,  $\langle P_1 \rangle$  and  $\langle P_2 \rangle$ , respectively. For ordinary non-ferroelectric nematics,  $\langle P_2 \rangle \neq 0$  and  $\langle P_1 \rangle = 0$ . For ferroelectric nematics, both  $\langle P_1 \rangle$  and  $\langle P_2 \rangle$  must be non-zero. In the case of an isotropic liquid both parameters,  $\langle P_1 \rangle$  and  $\langle P_2 \rangle$ , should be zero, if the system is infinite. The instantaneous second-rank order parameter  $P_2$  was taken to be the largest eigenvalue of the ordering matrix with the elements given by

$$Q_{\eta\xi} = N^{-1} \sum_{i=1}^N 2^{-1} (3n_{i\eta}n_{i\xi} - \delta_{\eta\xi}) \quad (2)$$

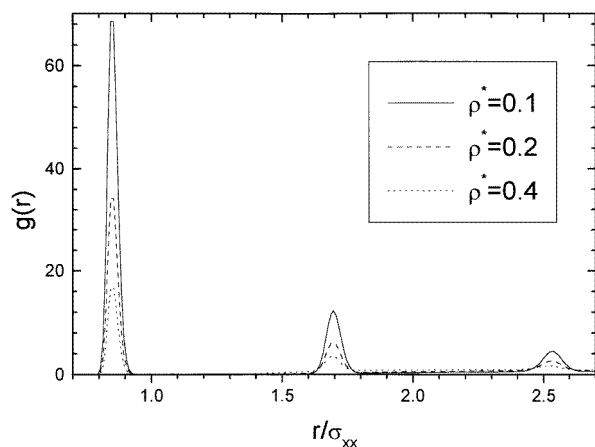
where  $n_{i\eta}$  is the  $\eta$ -component of the unit vector  $\mathbf{n}_i = \boldsymbol{\mu}_i / \mu_i$ . The corresponding eigenvector is the instantaneous director  $\mathbf{d}$ , and the instantaneous first-rank order parameter  $P_1$  is defined by

$$P_1 = N^{-1} \sum_{i=1}^N \mathbf{n}_i \cdot \mathbf{d}. \quad (3)$$

The equilibrium order parameters are the ensemble averages of  $P_1$  and  $P_2$ . The presence of ferroelectric order can be detected by calculating the average polarization per particle  $\langle P \rangle$  defined by

$$\langle P \rangle = N^{-1} \sum_{i=1}^N \mathbf{n}_i \cdot \mathbf{n} \quad (4)$$

where  $\mathbf{n}$  is a unit vector in the direction of the total instantaneous moment  $\boldsymbol{\mu} = \sum_{i=1}^N \boldsymbol{\mu}_i$ . Of course  $\langle P \rangle$  will be near zero for an unpolarized system and will approach 1 if the fluid becomes ferroelectric.



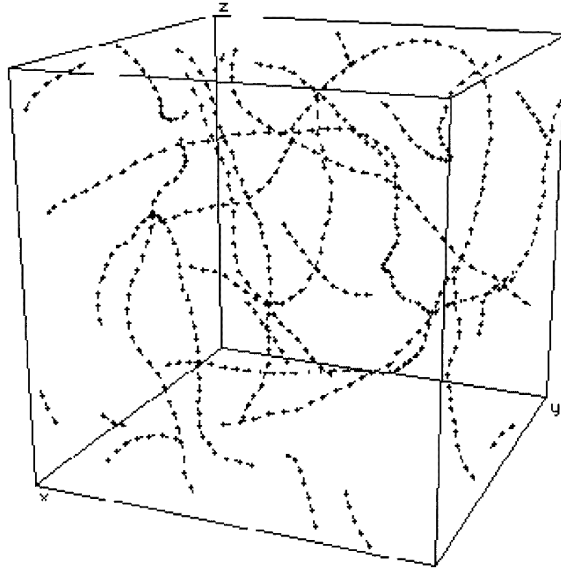
**Figure 3.** The central-core–central-core (X–X) radial distribution function  $g(r)$  for a range of reduced densities  $\rho^*$ .

**Table 1.** The equilibrium thermodynamic properties of an ensemble of strongly dipolar ( $\mu^* = 3.5$ ) linear molecules at the reduced temperature  $T^* = 0.0816$  as a function of the density  $\rho^*$ : the order parameters  $\langle P_1 \rangle$  and  $\langle P_2 \rangle$ , the polarization  $\langle P \rangle$ , the average number of molecules in a chain  $N_{\text{chain}}$  and the reduced potential energy  $-\langle U \rangle l^3 / N \mu^2$ . The maximal standard deviations for the order parameters and polarization are:  $\Delta P_1 = 0.03$ ,  $\Delta P_2 = 0.05$ ,  $\Delta P = 0.02$ .

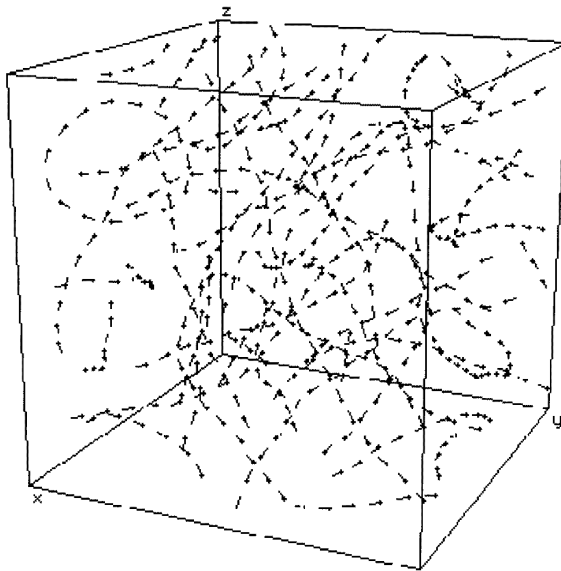
$\rho^*$	$\langle P_1 \rangle$	$\langle P_2 \rangle$	$\langle P \rangle$	$N_{\text{chain}}$	$-\langle U \rangle l^3 / N \mu^2$
0.050	0.13	0.16	0.14	266	4.73
0.100	0.12	0.13	0.14	83	4.73
0.125	0.10	0.17	0.12	115	4.73
0.150	0.09	0.13	0.09	83	4.73
0.175	0.10	0.16	0.16	83	4.73
0.200	0.12	0.18	0.15	125	4.73
0.300	0.11	0.15	0.16	100	4.72
0.400	0.10	0.13	0.18	148	4.70

We have also calculated the mean square displacement  $\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$  where  $\mathbf{r}_i(t)$  is the position of molecule  $i$  at time  $t$ . For fluids this quantity will continually increase with time, usually varying linearly at long times.

The mean square displacements are plotted in figure 2 and it is apparent that the system is a fluid for the densities studied,  $\rho^* \leq 0.4$ . The central-core–central-core (X–X) pair distribution functions  $g(r)$  are shown in figure 3 for a range of densities. Note that the position  $r_{\text{max}}$  of the first maximum of  $g(r)$  is shifted towards the lower value ( $r_{\text{max}} < \sigma_{XX}$ ) indicating the strong influence of attractive Coulombic forces.



**Figure 4.** A three-dimensional graph (snapshot) of an instantaneous configuration of 500 dipolar particles ( $\mu^* = 3.5$ ) at  $T^* = 0.0816$ ,  $\rho^* = 0.05$ . Arrows indicate the vectors of the dipole moments  $\mu_i$  ( $i = 1, \dots, 500$ ). The molecular axis of the  $i$ th particle (not shown in the graph to allow better visualization of the chainlike structure) is perpendicular to  $\mu_i$ .



**Figure 5.** A three-dimensional graph (snapshot) of an instantaneous configuration of 500 dipolar particles ( $\mu^* = 3.5$ ) at  $T^* = 0.0816$ ,  $\rho^* = 0.3$ .

The average number of molecules in a chain  $N_{\text{chain}}$  has been calculated using an energetically based criterion, as described in [6]: two molecules were considered to be

bound if their potential energy was lower than a predetermined value  $U_c = 0.7U_0$ , where  $U_0 = -2\mu^2/r_{\max}^3$ .

The results for the order parameters  $\langle P_1 \rangle$ ,  $\langle P_2 \rangle$ , the polarization  $\langle P \rangle$ , the average number of molecules in a chain  $N_{\text{chain}}$  and the reduced potential energy  $-\langle U \rangle l^3 / N \mu^2$  for the different thermodynamic states are summarized in table 1. The very small but non-zero values of  $\langle P_1 \rangle$  and  $\langle P_2 \rangle$  may result from the finite size of the simulated system and do not indicate the very weak ferroelectric nematic phase. When these results are supplemented with snapshots of instantaneous configurations, we observe very interesting behaviour of our system.

The striking finding is the formation of well defined molecular clusters which, by visual inspection, can be readily identified as being chainlike. Figures 4 and 5 show the instantaneous configurations of the system for a chosen density. Monomers are absent. It is important to note that a chain configuration evolves considerably during the MD run. A specific chain does not maintain a constant length, but can grow, break, and reform. Even rings or closed loops may appear (see figure 5). Each particular molecule is caught by some chain, and its individual mobility is substantially restricted. A typical chain consists of about hundred molecules ( $N_{\text{chain}} \simeq 80\text{--}140$ ); this implies a mesoscopic scale of spatial order in our system.

In summary, our simulations have shown that at least for certain boundary conditions an ensemble of elongated molecules with perpendicular dipoles can form spatially ordered, chainlike structures. That the tendency to form chains—with the dipole–dipole interaction ‘turned on’—can persist even in the presence of a quite complicated rotational dynamics stimulated by a three-site potential is an interesting finding. The fact that this can be accomplished with dipolar forces alone is perhaps mainly of theoretical interest, since in real liquid crystals other anisotropic interactions (short ranged) often dominate the dipolar contribution. However, we have shown that a spatially ordered phase generated by dipolar interaction alone can develop in systems that are more complex than those investigated earlier [1–6].

## Acknowledgments

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