## Chain Formation in Low Density Dipolar Hard Spheres: A Monte Carlo Study

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The phase diagram of dipolar hard spheres has been determined by Monte Carlo simulation for reduced densities  $\rho^*$  ranging from 0.02 to 0.3 and reduced temperatures  $T^*$  from 0.08 to 0.25. For  $T^* \leq 0.15$  the particles are found to associate to form chains which at the highest density are in a polarized ferroelectric state.

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It is only recently that the phase diagram of strongly interacting dipolar hard spheres has been investigated in some detail by computer simulations [1-3]. Both the low and high density regions have been considered. The calculations at low density [1], covering the density-temperature range (in reduced units)  $0.1 \le \rho^* = \rho \sigma^3 \le 0.4$ and  $T^* \ge 0.18$  [with  $T^* = 1/(\mu^*)^2$ ,  $\mu^* = (\mu^2/kT\sigma^3)^{1/2}$ where  $\mu$  is the dipole moment, T the temperature,  $\sigma$  the hard sphere diameter, k the Boltzmann constant], were directed towards the search of a liquid-gas transition. Somewhat surprisingly, these recent results point to the absence of such a transition in the  $(\rho^*, T^*)$  region considered in contrast with a number of theoretical predictions [4]. On the other hand, calculations at higher densities [2,3] ( $\rho^* \gtrsim 0.6$ ) have revealed that at sufficiently low temperatures (or high dipole moments,  $\mu^* \gtrsim 2.5$ ) dipolar hard spheres, as well as the related system of dipolar soft spheres [5], can form an orientationally ordered fluid phase. Furthermore, this ordered phase appears to be ferroelectric [3,5]. In addition, stable ferroelectric solid phases have been shown to occur as well [3,5].

The purpose of this Letter is to report Monte Carlo (MC) calculations extending the previous ones to still lower densities ( $\rho^* = 0.02-0.3$ ) and temperatures ( $T^* = 0.082-0.25$ ). The most striking finding is the formation, at low temperature, of well defined chains which at the highest densities considered are in a polarized ferroelectric state.

The MC simulations were performed in the canonical ensemble for a system of N = 500 particles in a cubic box repeated periodically in space. The long range dipolar interactions were accounted for using the Ewald method. The total internal Ewald energy is the sum of periodic pair potentials between the particles and a term proportional to  $M^2$ , the square of the total electric dipole moment of the system [6]. This last term is combined with the reaction field contribution of a continuous dielectric medium of dielectric constant  $\epsilon'$  supposed to surround the (infinitely) large sphere filled with the periodic replica of the basic simulation cell. The resulting contribution to the total Ewald energy is  $2\pi \mathbf{M}^2/(2\epsilon'+1)V$ , where V is the volume of the system [6]. In the present study we made the choice  $\epsilon' = \infty$  which thus eliminates the contribution to the energy arising from the depolarization field

and fully specifies the boundary conditions used in our simulations [3].

A MC trial move combines displacement of a hard sphere center and rotation of its dipole moment. The acceptance ratio varied between 0.2 and 0.5, depending on temperature and density. Even at the lowest temperatures considered substantial diffusion of the particles was observed, a prerequisite for adequate sampling of phase space.

The behavior of the system at low temperature is characterized by association of the dipolar spheres to form clusters which, by visual inspection, can be readily identified as being chainlike. However, to characterize quantitatively these chains a precise working definition of a chain is required. Among the possibilities of using either a sterically or an energetically based criterion, the latter turned out to be the most adequate. This criterion has the advantage to take into account the two main features of chain formation in the dipolar hard sphere system: proximity of neighboring particles and alignment of their dipole moments. This last aspect would be fully neglected by a criterion based on particle distances only. Two spheres were considered to be bound if their potential energy was lower than a predetermined value  $U_c$ , chosen to be  $-1.4(\mu^*)^2$  in reduced units [note that the lowest energy of a pair of dipolar hard spheres at contact is  $-2(\mu^*)^2$ ]. This choice of  $U_c$  was guided by the analysis of a number of instantaneous configurations of the system and record of the average values of the first, second, and third lowest pair energies  $\overline{E}_1, \overline{E}_2, \overline{E}_3$  of each particle. Here we can already note that, when aggregation occurred, the values of  $\overline{E}_1$  and  $\overline{E}_2$  were close but considerably lower than  $\overline{E}_{3}$ , indicating chain formation rather than formation of more compact clusters (in which case all three values of  $\overline{E}$  would have been close). For example, at  $\rho^* = 0.1$ ,  $\mu^* = 3.5$ , one finds  $\overline{E}_1 = -22.16$ ,  $\overline{E}_2 = -19.17$ , and  $\overline{E}_3 = -3.56$ .

Chains were then identified as follows: For each particle *i*, in a given configuration, denote by  $E_{ij}^{(1)}$  and  $E_{ik}^{(2)}$  the energies of the pairs (i,j) and (i,k) having the first and second lowest energies. Choose a particle at random, say *i*, and assume that it does not yet belong to a chain. If  $E_{ij}^{(1)} < U_c$ , particle *j* will belong to the chain. Move to particle *j*. If  $E_{ij}^{(1)} < U_c$ , particle *l* is accepted as the next

TABLE I. Dipolar energy  $U_d/NkT$ , order parameter S, polarization P, average number of spheres in a chain  $\bar{n}_l$ , average persistence length  $\bar{l}_p$ , and number of monomers of a system of 500 dipolar hard spheres as a function of density and temperature. The error on  $U_d/NkT$ , S, and P is of the order of (2-3)%, on  $\bar{n}_l$  and  $\bar{l}_p$  of the order of 10%. For all thermodynamic states the pressure is nearly zero.

 ρ*		μ*	Moves/N	U <sub>d</sub> /NkT	S	Р	<i>n</i> <sub>l</sub>	$\bar{l}_p$	Mono
0.30	0.25	2.0	35 000	-5.1	0.04	0.04	2.7	• • •	180
0.30	0.16	2.5	30 000	-11.9	0.09	0.38	5.2	4.0	20
0.30	0.1111	3.0	30 0 0 0	-18.7	0.38	0.70	16.5	10.9	3
0.30	0.0816	3.5	40 000	-26.5	0.40	0.71	27.0	18.2	0
0.20	0.0816	3.5	40 000	-25.8	0.12	0.48	24.6	6.7	0
0.10	0.25	2.0	40 000	-3.9	0.04	0.03	2.6		200
0.10	0.16	2.5	40 000	-11.0	0.11	0.40	6.7	3.9	20
0.10	0.1111	3.0	40 000	-18.1	0.11	0.44	24.5	8.8	0
0.10	0.0816	3.5	30 000	-25.0	0.11	0.44	24.2	7.3	0
0.05	0.0816	3.5	40 000	-25.4	0.05	0.10	30.4	3.3	0
0.02	0.25	2.0	20 000	-1.8	0.04	0.03	2.3		350
0.02	0.0816	3.5	30 000	-24.0	0.05	0.13	8.4	4.3	0

member of the chain provided it does not yet belong to it or to another chain. Otherwise the energy criterion is checked for  $E_{jm}^{(2)}$ . The process is continued until the chain stops (energy criterion not satisfied or neighbor belonging already to a chain). Then move back to the initial particle *i* and check the energy criterion for  $E_{in}^{(2)}$ (second lowest pair energy) in order to grow the chain in the opposite direction. We note that the preceding chain definition, based on consideration of only the first two lowest pair energies, obviously does not allow for branched chain configurations. In fact, in the density region over which the chain concept seems meaningful, such configurations would occur only very rarely.

Having adopted this definition of a chain, we calculated the average number of spheres,  $\bar{n}_l$ , in a chain and a (average) persistence length from

$$\bar{l}_p = \sum_{k=1}^{n_l-2} \langle \mathbf{e}_1 \cdot \mathbf{e}_{1+k} \rangle \tag{1}$$

averaged over all chains with  $n_l > 10$ . In Eq. (1),  $\mathbf{e}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$  denotes a vector joining two successive hard sphere centers and  $n_l$  the number of spheres in a chain. Averages were taken over independent configurations spaced by 2000 trial moves/particle.

Furthermore, we calculated an order parameter S defined as the average value of the largest eigenvalue of the second rank tensor

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} \left( 3\hat{\mathbf{u}}_i \hat{\mathbf{u}}_i - \mathbf{I} \right)$$
(2)

and a possible polarization of the system from

$$P = \frac{1}{N} \left\langle \left| \sum_{i=1}^{N} \hat{\mathbf{u}}_{i} \cdot \hat{\mathbf{d}} \right| \right\rangle, \qquad (3)$$

where  $\hat{\mathbf{u}}_i$  is a unit vector in the direction of the dipole moment  $\boldsymbol{\mu}$  and  $\hat{\mathbf{d}}$  the director of the system defined as the instantaneous eigenvector associated with the largest eigenvalue of Q.

Results for the internal energy, order parameter, polarization, average number of particles in a chain, and persistence length of the different thermodynamic states are summarized in Table I. When supplemented with snapshots of instantaneous configurations of the system, the following behavior becomes apparent as a function of density and temperature.

Formation of chains occurs most strikingly in the density region  $\rho^* = 0.05 - 0.2$  and for temperatures  $T^* \leq 0.15$ . In this region the density is sufficiently low for the



FIG. 1. Snapshot of a configuration of 500 dipolar hard spheres at  $\rho^* = 0.1$ ,  $T^* = 0.0816$  ( $\mu^* = 3.5$ ) (projection of the dipole moments on the y-z plane of the periodic simulation cell). The association of the dipolar spheres into chainlike structure is clearly visible. The dipole moments are represented by thin lines of length  $0.8\sigma$ . The hard sphere centers are in the middle of the lines. The symbol for the head of the dipole moments varies with number of spheres  $n_l$  in the chain. Open circles:  $1 \le n_l < 10$ ; squares:  $10 \le n_l < 20$ ; triangles:  $20 \le n_l < 30$ ; solid circles:  $n_l \ge 30$ . Distances are in unit of  $\sigma$ .



FIG. 2. Three-dimensional graph of an instantaneous configuration of 500 dipolar hard spheres at  $\rho^* = 0.1$ ,  $T^* = 0.0816$  ( $\mu^* = 3.5$ ). Chains with different numbers of spheres are represented with different gray levels.

method of chain analysis described above to be applicable in an unambiguous way. Figure 1 shows an instantaneous configuration of the dipolar spheres at  $\rho^* = 0.1$ ,  $T^* = 0.0816 \ (\mu^* = 3.5)$  projected on the y-z plane of the simulation box; a three-dimensional view of the system is given in Fig. 2. At this temperature  $(T^*=0.0816)$  the average number of spheres in a chain (which, for short, we will call chain length, although it should be stressed that the spheres in a chain are not strictly in contact) is  $\sim$ 25; a chain may comprise, however, as many as a hundred spheres. Monomers are absent. (A detailed analysis of the distribution of chain lengths will be postponed until publication of a fuller description of this work.) It is important to remark that a chain configuration evolves considerably during the MC run. A specific chain does not keep a constant length but can grow, break, and reform. In the density range  $\rho^* = 0.05 - 0.2$  the average chain length does not vary appreciably (at fixed temperature), only near  $\rho^* = 0.02$  does it start to drop more rapidly due to an increase of the number of small chains and monomers. The persistence length  $\bar{l}_p$  is constant  $(\bar{l}_p \sim 7)$  at  $\rho^* = 0.2$  and 0.1 (cf. Table I) then decreases to 3 for  $\rho^* \sim 0.05$  indicating a more winding nature of the chains. At all densities considered the chain phase disappears rather abruptly at  $T^* \sim 0.15$  giving rise to an ordinary fluid phase (cf. Fig. 3). The difference in phase behavior of the system on either side of the isotherm  $T^* \simeq 0.15$  is also quite visible on the values of the internal energy (cf. Table I). At low temperature the energy of the system is remarkably constant with density (at a given temperature) and is dominated to within 90% by intrachain (nearest neighbor) pair interactions, while at high temperature the decrease of energy with density is pro-



FIG. 3. Snapshot of a configuration of 500 dipolar hard spheres at  $\rho^* = 0.1$ ,  $T^* = 0.25$  ( $\mu^* = 2.0$ ) (projection of the dipole moments on the y-z plane of the periodic simulation cell). Symbols are as in Fig. 1.

nounced.

At  $\rho^* = 0.3$ , the higher density of the system renders our definition of chains more dubious to apply. Nonetheless, for temperatures  $T^* \leq 0.15$  we identify chains of lengths comparable to those determined at lower density (cf. Table I). A striking difference with the low density case is, however, that the system is now polarized (cf. Fig. 4). This finding is consistent with the ferroelectric behavior of the system observed previously [3] at still higher densities [although at these higher densities ( $\rho^* \gtrsim 0.7$ ), obviously, no chains can be identified anymore in the system]. Because of the polarized nature of the chains these stretch more linearly than in the low density



FIG. 4. Snapshot of a configuration of 500 dipolar hard spheres at  $\rho^* = 0.3$ ,  $T^* = 0.0816$  (projection of the dipole moments on the y-z plane of the periodic simulation cell). The system is polarized along the z axis of the simulation cell. The symbols are as in Fig. 1.

case, a result corroborated by the larger value of the persistence length (cf. Table I). From Table I it is apparent that both chain formation and polarization vanish at temperatures  $T^* \gtrsim 0.15$ . One also sees that a weak reminiscence of polarization is also present at lower densities. Notice that a value  $P \approx 0.4$  corresponds to a low value of the order parameter S since for a uniformly polarized state P is roughly  $\propto \sqrt{S}$ .

The physical system which approaches most closely the present highly idealized one is maybe the ferrofluid system. Ferrofluids are colloidal suspensions of magnetic particles (50-100 Å) in various carrier liquids [7]. At low temperatures ferrofluids are known to aggregate to form chains [8] although this requires the presence of an external magnetic field. Our results seem to indicate that such formation could be spontaneous for adequate values of the magnetic moments of the particles.

We finally remark that in the  $(\rho, T)$  domain investigated in the present work (extending appreciably that considered in Ref. [1]) no tendency for a liquid-gas transition is evident. For systems undergoing a liquid-gas transition, as is, for instance, the case for the Stockmayer potential, the phase diagram is possibly even more complex than for the present model due to an interplay of the tendencies of chain formation and liquid condensation [9].

A full account of the phase diagram of dipolar hard spheres including extension to a wider density-temperature domain as well as a theoretical analysis will be given in a future publication.

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