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Structure and Dynamics of a Dense Dipolar System in an Electric Field and Their Relevance to Electrorheological Fluids

N. K. Jaggi[1]

Results of computer simulations of a dense system of dipolar spheres in an electric field are summarized. Dissipative and Hamiltonian dynamics algorithms have been used to find energy minima of the system for varying particle densities. The structures obtained by these simulations are in reasonable agreement with experimentally observed structures in electrorheological (ER) fluids. Qualitative agreement is also obtained with the limited available experimental observations on the dynamics of ER fluids.

KEY WORDS: Dipolar fluids; Electrorheological; structure; dynamics.

1. INTRODUCTION

During the last 3 years, different groups[1-9] have studied the fundamental physics of electrorheological (ER) fluids and independently arrived at a model in terms of a colloidal suspension of highly polarizable solid particles in low-dielectric-constant fluids, along with the appropriate hydrodynamic interactions. The yield stress of the solid that forms in the presence of an electric field above a threshold[1,2] value E_c has been estimated[7] assuming that the induced structure consists of independent chains of dielectric particles spanning the electrodes. This approximation of the structure is frequently used and is supported qualitatively by recent computer simulations.[3,4]

One of the unresolved problems is the following. Optical microscopy of two- and three-dimensional suspensions of microspheres in electric fields has shown[7-9] that the structures are rarely chainlike. At typical densities

[1] Department of Physics, Illinois Wesleyan University, Bloomington, Illinois 61702 and Northeastern University, Boston, Massachusetts 02115.

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where finite yield stresses exist in the presence of an electric field, the observed structures are correctly described as thick columns[7,8] or fibrils as they are often referred to. Also, these columns that span the electrodes are far from being uniform. They often exhibit cross-linking and constrictions,[8] the width of the columns varying significantly as one moves along the field direction between the electrodes. Computer simulations[3] referred to above do not agree with these experimental observations. The simulations found either single chains or double-width strands.

On the other hand, our mean field analysis[1,2] of the free energy of a dipolar gas in an electric field predicts that the osmotic pressure of the particle system becomes negative above a critical electric field $E_c(T)$. Therefore, at sufficiently low temperatures or at sufficiently high electric fields, the system should have a tendency to phase-separate. Obviously, a mean field analysis that ignores axial anisotropy cannot predict the structure of the high-density phase that would result from this phase separation. Its predictions regarding the detailed nature of the transition[1] must also be considered tentative unless verified by a more precise analysis.

2. SCOPE OF THIS WORK

This paper has a narrowly defined goal. In particular, we have nothing to say about what happens in the presence of shear, the subject of important earlier simulations[4] which simulate a small number of particles (25) but treat the hydrodynamics carefully. We also make no claims about the appropriateness or otherwise of other models of ER behavior. The only question being asked is the following. Is the microscopic phase separation, viz. the formation of thick columns, as seen by experiments[7-9] and expected from our earlier mean field analysis,[1,2] consistent with computer simulations of the dipolar gas model?

New results of our computer simulations of a two-dimensional dipolar gas model are summarized. Even though the models differ in apparently small details, they seem to have noticeable effect on the resulting structures. Some qualitative comments are also offerred regarding metastable local minima, allowing for some hard-sphere overlap at intermediate steps of the simulation and the possible importance of choosing a cutoff of the dipolar interaction.

We do find a structure that is in qualitative agreement with experiments.[7,8] It is anisotropic, long-range percolated, microscopically phase-separated and has local regions of imperfect triangular lattice ordering.

3. THE MODEL

Our system consists of a given density of polarizable hard spheres of diameter σ, each having an induced dipole moment p along the direction of the applied electric field E. In a complete theory, this induced dipole moment must be determined self-consistently, taking into account the structures being formed, as has been attempted earlier.[5] In all the simulations referred to[3,4] and in the present work, this is considered to be a renormalizable parameter which sets the energy and therefore time scale, but does not affect the resulting structure. The spheres are assumed to be neutrally buoyant in a dielectric fluid medium having a viscosity η_c, contained between parallel metallic electrodes with a spacing of $L_z\sigma$ maintaining an electric field E along the z axis.

The dynamics of this system is given by the following equation:

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i U(\{\mathbf{r}_j\}) - 3\pi\eta_c\sigma\frac{d\mathbf{r}_i}{dt} \tag{1}$$

where the total electrostatic energy $U(\{\mathbf{r}_j\})$ is approximated by the dipolar form

$$U(\{\mathbf{r}_j\}) = -p^2\sum_{\{ij\}}\frac{(3\cos^2\theta_{ij}-1)}{r_{ij}^3} \tag{2}$$

In the simulations we directly use the expression for the electrostatic force $\mathbf{F}_i$ on the ith dipole

$$\mathbf{F}_i = -\nabla_i U(\{\mathbf{r}_j\}) = 3p^2\sum_j\frac{1}{r_{ij}^4}[(3\cos^2\theta_{ij}-1)\,\hat{e}_r + (\sin 2\theta_{ij})\,\hat{e}_\theta] \tag{3}$$

The sum runs over all dipoles and their sequence of images in the two metallic electrodes.

The two approximations made in writing these equations deserve comment. A more sophisticated treatment of the hydrodynamic forces is necessary for a complete description of the flow properties and has in fact been used in the literature.[4] But since all velocities are zero in the ground state, the present simplification has no effect on the equilibrium structure and therefore also on the static yield stress that may be computed for these structures.

Multipolar corrections may also be important in determining fine details of the observed structures. But in this and earlier[3] work, these are ignored.

Let us consider two limiting cases of Eq. (1). With the viscous term set

to zero, we have the many-body Hamiltonian of a classical, dense dipolar gas in an electric field

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i U(\{\mathbf{r}_j\}) \tag{4}$$

The ground-state and finite temperature properties of this system can be computed within the framework of equilibrium statistical mechanics.

The other limiting case is the noninertial, fully dissipative equation which is obtained by setting the left-hand side of Eq. (1) to zero,

$$3\pi\eta_c\sigma\frac{d\mathbf{r}_i}{dt} = -\nabla_i U(\{\mathbf{r}_j\}) \tag{5}$$

If the electric field and the viscosity of the carrier fluid are sufficiently large and the temperature is sufficiently low, the noninertial equation (5) can be a rather good approximation for ER fluids. However, for fine particles, at smaller electric fields, at higher temperatures, or for small viscosity of the continuous medium, all the terms must be preserved and Brownian forces must also be included at equal footing to understand the structures and dynamics.

4. EQUILIBRIUM STRUCTURES FROM DISSIPATIVE DYNAMICS

Our primary goal is to find structures that are energy minima of this classical interacting system; i.e., $\{\mathbf{r}_j\}$ that minimizes the dipolar interaction energy $U(\{\mathbf{r}_j\})$. Since the minima of energy are attractors of the dynamics in phase space, it should be possible to obtain the ground state by investigating the dynamics of either the inertial equations of motion (4) or that of the noninertial, fully dissipative equations of motion (5).

The simplest way, at least in principle, to obtain the ground state is to integrate Eq. (5) starting from any starting random configuration $\{\mathbf{r}_j\}$. In this paper, lengths and times are normalized and are given in the natural units of the particle diameter σ and $t^* = \pi\eta_c\sigma^6/p^2$, respectively. Numerically precise integration of Eq. (5) for a sufficiently long time is guaranteed to take the system into a minimum of the total energy. In earlier simulations,[3] the Euler method was used with very small values of the time step $\delta t = 0.001$ and the dipolar interaction was cut off at $r_c = 5$.

The present simulations differ from the previous ones[3,4] in some apparently small details, which nevertheless seem to have noticeable effect on the resulting structures. These are discussed in the following.

First, for complex anisotropic interactions of the kind under consideration here, one must anticipate the possibility of many local energy minima in phase space. And numerically precise integration of Eq. (5) guarantees that the system gets permanently trapped in the local minimum which is nearest to the starting configuration. This is highly unlikely to be representative of either the global minimum or even the structures that form in real systems, where damping is finite and inertial and Brownian forces are nonzero. Our simulations using third-order Runge-Kutta with $\delta t = 0.005$ and earlier simulations[3] using the Euler method with $\delta t = 0.001$ lead to very similar structures of ER fluids.

The brute-force approach to finding the deepest minimum will then consist of starting from many different initial configurations $\{\mathbf{r}_j\}$; integrating Eq. (5) precisely with very small δt till they get to the nearest local minimum; computing the total energies in all these local minima; and looking for the deepest minimum. In this case, the computation time goes as $\sim n^2 N_m T/\delta t$, where N_m, n, and T, respectively, indicate the number of local minima obtained, the number of particles, and the total time over which the simulation is carried out.

The algorithm used here is a slight modification of the above approach, but results in significant savings of computation time and allows us to extend simulations for much longer total times T. It consists of a two-step integration. Since we do not want to get trapped in the nearest local minimum encountered, we first intentionally use the Euler method with a moderately large time step Δt so that the system can skip over, without getting trapped in, shallow minima or those minima whose basin of attraction is not too wide. During this part of the simulation, the electrostatic energy decreases monotonically at first and then starts oscillating. The actual trajectory in this simulation does not accurately represent real dynamics and sometimes has the unphysical, finite penetration of the particles a little bit inside the hard core. When as a result of updating the positions, spheres penetrate into each other, this overlap is corrected by moving the spheres apart along the line joining their centers. Many of the configurations generated toward the end of the first coarse simulation are used as starting configurations for a second series of numerically precise simulations. At the beginning of this second simulation, any overlap of the hard cores is removed by moving the particles radially apart, and the system is allowed to evolve further using a much smaller time step δt to try to fall into the nearest minimum. In the present simulations, Δt was 50–100 times larger than δt. The computation time for this mode of calculation is $\sim n^2[T/\Delta t + N_m \Delta T/\delta t]$.

It is not particularly enlightening to present our results in detail unless one can produce an animation. In the following, therefore, we summarize

the key features. We always employ periodic boundary conditions along the y axis and of course carry the dipole images along the electric field z axis. The interaction cutoff distance ranges from a minimum of 20 up to 80 in some runs, but is never less than $2L_z$.

We would like to point out that this may be of some importance. It is obvious that the first-order effect of the dipolar interaction in a dilute system is to line up particles along chains in the direction of the dipole moment. However, in concentrated systems, as the present simulations and real ER fluids are, the coarse scale structure can be strongly affected by the effective interactions between chains and chain segments that are forming. In particular, cutting off the dipolar interaction at less than $2L_z$, as was done in earlier simulations, partially decouples the dipoles and their images in the electrodes. Resulting structures could then be qualitatively different.

Figure 1 shows the configuration of a system of 252 particles in a 40×10 $[L_y \times L_z]$ toward the end of one of the simulations. In all cases, the first coarse integration was carried out with $\Delta t = 0.05$ and the final fine integration was carried out with $\delta t = 0.0005$. Thus, for example, the indicated configuration at $t = 200$ is obtained by integrating for 3996 steps using $\Delta t = 0.05$ to get to $t = 199.8$ followed by 400 steps using $\delta t = 0.0005$.

The structures obtained are in reasonable agreement with what has been observed in real ER fluids using optical microscopy.[7,8] In particular, the following aspects are common between experimental structures and present simulations.

1. There is clear directional percolation of particles spanning the electrodes. This explains the ability to transfer shear stress from one electrode to another even at zero strain rate, viz. its solidlike behavior.

2. The structures are far from chainlike: they consist of thick columns of particles. The simulations are not extensive enough to establish a quantitative relation between column thickness and electrode spacing, but do suggest that for a given dipole moment (which in turn means a given electric field), larger interelectrode spacing leads to thicker columns. This would make the agreement with observed structures even better.

3. There are regions that are devoid of particles and contain just the continuous medium. The microscopic tendency to phase-separate is obvious.

4. The columns themselves are not straight and lined exactly along the field. They clearly show necking and also some bending and cross-linking between columns. Thus the interface between the high-density regions and the low (nearly zero)-density regions is rough, but aligned predominantly along the field axis.

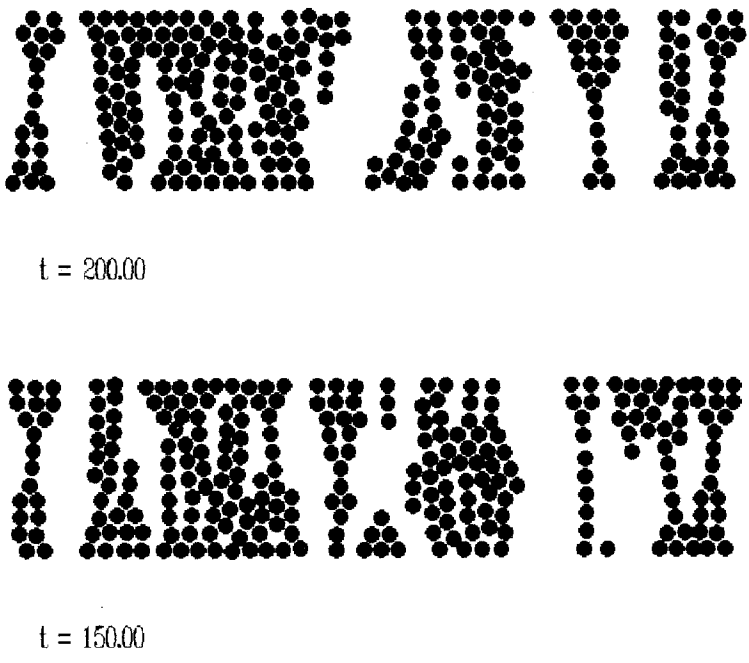

Fig. 1. Two of the lowest energy structures obtained using the modified dissipative dynamics algorithm as described in the text. $n = 252$ particles, $L_z = 10$, $L_y = 40$.

One feature that is seen in the simulated structure but not yet observed experimentally is the tendency of particles within the thick columns to be close-packed. In the present two-dimensional simulations, this leads to a triangular lattice-like structure within the columns. By analogy, in three dimensions, the columns may be expected to have locally fcc- or hcp-like ordering. Any distribution of sphere diameters will of course tend to destroy this.

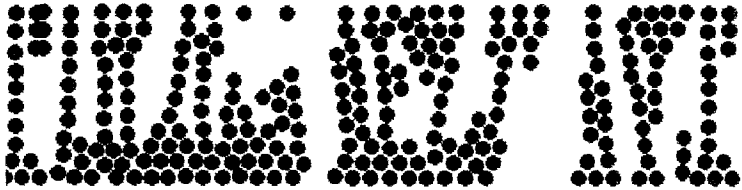

Fig. 2. Structure obtained by "cooling" the microcanonical ensemble (see text) from a very high temperature. $n = 252$ particles, $L_z = 10$, $L_y = 40$.

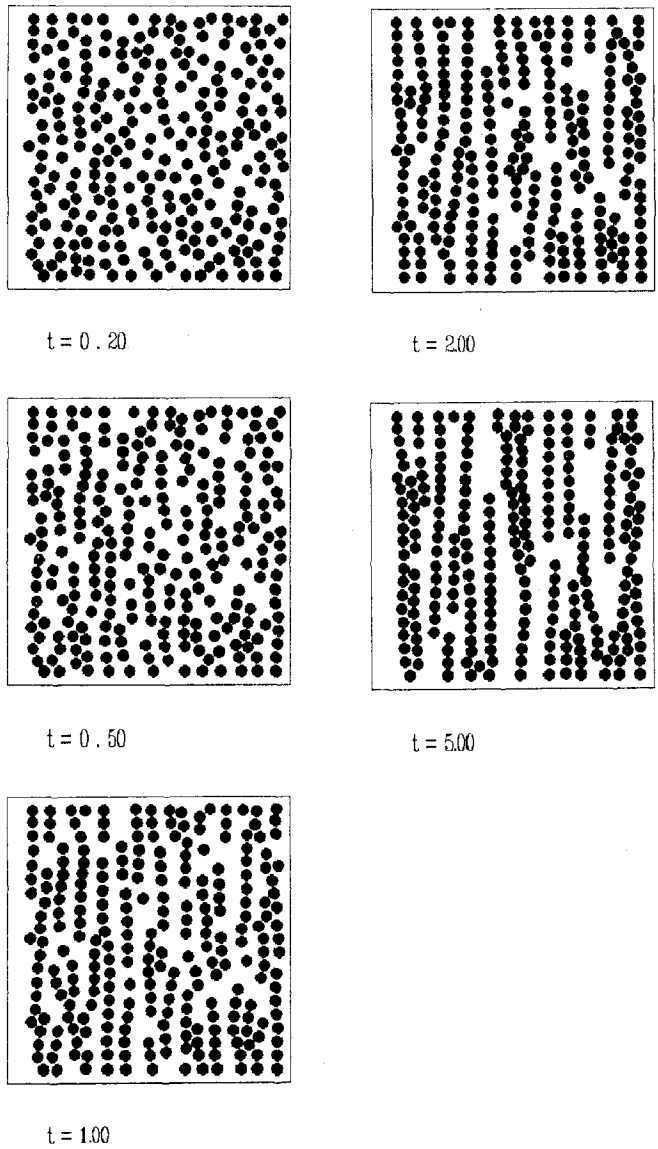

Fig. 3. Dynamic response of typical ER fluids. $n = 252$ particles, $L_z = 20$, $L_y = 20$, time is in units of $t^* = \pi\eta_c\sigma^6/p^2$.

5. GROUND STATE USING HAMILTONIAN DYNAMICS

If one starts the system from any arbitrary configuration at rest and lets it evolve under the Hamiltonian equations of motion (3), the interactions soon redistribute part of the potential energy as the kinetic energy of the particles, equivalent to a microcanonical ensemble with a given total energy. The standard trick used in MD studies of phase transitions is to continue to remove kinetic energy from the system, by a downward rescaling of all speeds during the iteration, to reduce the temperature of the system. The size and frequency of this rescaling of speeds determine an effective cooling rate. If the system is cooled sufficiently "slowly," one expects to find the ground-state structures.

Figure 2 shows the structure obtained when the same system as in Fig. 1 was "cooled" in the sense described above, from a very high temperature to a very low (but nonzero) temperature. The resulting structure has essentially the same features as found earlier. This is reassuring.

6. DYNAMIC RESPONSE

Klingenberg *et al.*[3] showed that for typical engineering ER fluids under high fields of the order of 1–2 kV/mm and for typical values of η_c, the dynamic response of the ER fluids to the applied field can be well approximated by the noninertial equations of motion (4). In particular, they found in their simulations that chainlike structures form in $t \sim 1$ (in units of t^*) for the case they studied. From known material constants, they estimated t^* for typical ER fluids under typical conditions to be of the order of 10^{-3} sec. This was the first microscopic understanding of the following important, though imprecise, experimental observation: the response time of ER fluids is often as little as a few milliseconds.

Figure 3 shows a representative sequence of configurations from our simulations for $n = 252$ particles in a 20×20 system at times $t = 0.2$, 0.5, 1.0, 2.0, and 5.0. The initial configuration at $t = 0$ was a random one with the constraint of no particle overlap, corresponding to the time when the electric field is turned on. It is found that chainlike structures, with a distribution of chain lengths, some of them as large as the interelectrode spacing, do indeed form at around $t = 2$. It is similar to earlier simulations[3] at comparable densities and in qualitative agreement with experiments. It is included to indicate the dynamics of these complex fluids.

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