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NON-EQUILIBRIUM STRUCTURE OF ROTATIONALLY DRIVEN DIPOLES: THE ROLE OF THE SIMULATION METHOD

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Dipolar colloidal particles in a rotating biaxial field tend to form layer-like structures in the plane of the field. In this manuscript, we compare Molecular dynamics (MD) and Brownian dynamics (BD) simulations results of rotationally driven dipoles. Our goal is to understand the differences in the dynamics predicted by these two simulation methods when the strength and the driving frequency of the field are varied. In particular, we compare the layer formation behaviour in MD and BD by investigating its breakdown at a constant field strength and its onset at a constant rotational frequency of the field.

Introduction. Particles that are driven by time-dependent fields currently receive a lot of attention. Studies in this area focus, on the one hand, on the field-induced dynamics of isolated nanoparticles [1–4] and, on the other hand, on the self-assembly behaviour in colloidal many-particle systems. The latter is very important in material science, where time-dependent fields are an important tool for synthesizing functional materials [5, 6]. A classical example in this context, first discussed by Martin *et al.* [7], are systems of paramagnetic (or polarizable) spherical particles in magnetic (electric) fields rotating in a plane. For sufficient field strength, both experiment and computer simulations [7–9] reveal the field-induced formation of layers in the plane of the field.

The physical reason for this structure formation phenomenon is the synchronized rotation of the dipole moments with the field and, hence, with one another. On averaging over time, this rotation results in an "inverted" dipolar interaction, which is attractive within the plane of the field and thus, favours layering [9, 10].

For particles with induced dipole moments, such as paramagnetic or polarizable particles, the synchronized rotation is clearly given. The (rotational) motion of particles with permanent dipoles, where the individual orientation of a particle can differ from the field, is less clear. However, as was first shown by Murashov and Patey [11], the layering phenomenon persists for permanent dipoles.

In a recent study [12], we have explored in detail the layer formation and rotational dynamics of systems of permanent dipoles for a broad range of driving parameters. To this end, we have employed BD computer simulations supplemented by a theoretical approach. A characteristic feature of the BD method is that the particles are subject to certain non-conservative (i.e. friction and random) forces and torques in addition to the usual conservative ones. Therefore, with the given non-equilibrium character of the phenomena of interest, it is an important question how the dynamic behaviour would change with a different choice of the equations of motion. This is precisely the goal of the present study, where we compare the layering and synchronization behaviour observed in BD with that emerging in corresponding MD simulations, which lack the Brownian non-conservative forces and

torques. To highlight the differences, we restrict ourselves in the present study to the investigation of some particularly interesting state points.

1. Model and simulation methods. The system we consider here is comprised of colloidal particles, which carry a permanent dipole moment. In our simulations, we model this colloidal suspension by a system of dipolar soft spheres (DSS) without taking the solvent explicitly into account. The DSS pair potential between two spheres consists of a repulsive part, a soft sphere potential, and a point dipole-dipole interaction potential [12].

We use MD simulations in the canonical ensemble and non-overdamped BD simulations to investigate the system. The details of the former technique are described, e.g., in [13], while BD simulations are described in [11, 12]. Note that we use a Gaussian isokinetic thermostat in our MD simulations. In BD, the temperature is maintained by the balance of frictional and random forces (and torques).

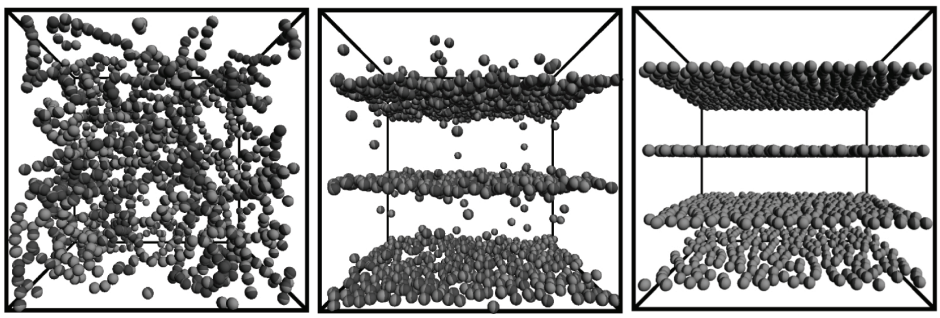
The external field that the particles interact with rotates with the frequency ω_0 in the (x, y)-plane and is given by

$$\mathbf{B}(t) = B_0(\mathbf{e}_x \cos\omega_0 t + \mathbf{e}_y \sin\omega_0 t). \tag{1}$$

Reduced units are used for the field strength $B_0^* = (\sigma^3/\epsilon)^{1/2} B_0$ and angular frequency $\omega_0^* = (m\sigma^2/\epsilon)^{1/2}\omega_0$. Here, m is the mass of the particles and σ and ϵ are parameters, which appear in the soft sphere potential, representing the diameter of the particles and providing a typical energy scale. Further, the density was chosen to be $\rho = 0.1 \cdot \sigma^{-3}$, the moment of inertia as $I = 0.025 \cdot m\sigma^2$, the temperature as $T = 1.35 \cdot \epsilon/k_B$, the dipole moment as $\mu = 3 \cdot (\epsilon\sigma^3)^{1/2}$, and the translational and rotational diffusion constants as $D = 0.1 \cdot (\epsilon\sigma^2/m)^{1/2}$ and $D_r = 3 \cdot (m\sigma^2/\epsilon)^{-1/2}$, respectively. A timestep of $\Delta t = 0.0025 \cdot (m\sigma^2/\epsilon)^{1/2}$ was used and the simulations were carried out with 864 particles. These values are consistent with those chosen in earlier computer simulation studies of rotating dipolar systems [11, 12].

2. Layering and synchronization in MD and BD. The zero field system that represents our starting point is strongly coupled (with the coupling strength $\lambda = \mu^2/(k_B T\sigma^3) \approx 6.7$) and of relatively low density ($\rho\sigma^3 = 0.1$). A typical snapshot revealing the equilibrium structure of the system can be seen in Fig. 1*a*.

Exposing this system to a rotating field of suitable strength B_0 and frequency ω_0 leads to the formation of layers in the plane of the field. Exemplary, this can be seen in Figs. 1*b* (BD) and 1*c* (MD).



(*a*) (*b*) (*b*)

Fig. 1. (*a*) Snapshot of the system in zero field (BD). (*b*) Snapshot from a BD simulation of a system in a layered state. The strength and frequency of the field are $B_0^* = 12$ and $\omega_0^* = 15$, respectively. (*c*) Snapshot from a MD simulation of a system in a layered state ($B_0^* = 12$, $\omega_0^* = 10$).

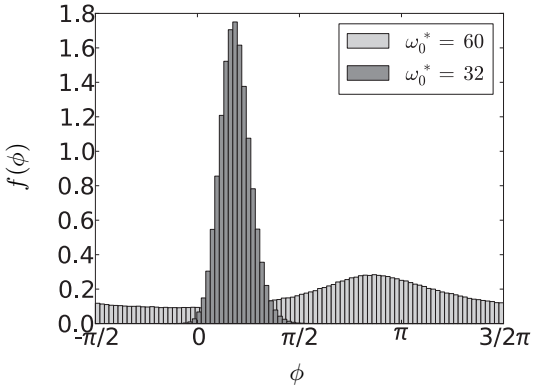


Fig. 2. Distribution of the phase differences at $B_0^* = 10$ and two frequencies ω_0^* (BD). The system at $\omega_0^* = 32$ is in a layered state, the other one is not.

To distinguish between systems in layered and unlayered states, we need an order parameter. Here we use the one introduced in [12], which is given by

$$\psi = \frac{1}{N} \sum_{i=1}^{N} \langle n_i \rangle. \tag{2}$$

In Eq. (2), N is the total number of particles, $\langle \cdots \rangle$ denotes a time-average, and n_i is defined as follows. Consider a sphere of radius $r_0 = 8\sigma$ around a particle i. Divide that sphere into two parts, one of which is given by the points within the sphere, whose distance vector to the particle i together with the z-axis encloses an angle Θ satisfying $-0.5 < \cos\Theta < 0.5$. If there are more (less) particles in this equatorial volume than in the polar volume around the particle i, set $n_i = 1$ (-1); if there is the same number of particles, set $n_i = 0$. Also we consider a system layered if $\psi \geq 0.6$. A full non-equilibrium phase diagram in the (ω_0, B_0)-plane based on the order parameter ψ has been presented in [12].

On a microscopic (particle) level, the layering is caused by synchronous rotation of the particles with the field [11, 12]. This can be seen in Fig. 2, where, for a layered system, the distribution of the phase differences between the direction of the field and the particles is shown to have only a single isolated peak. Hence, the particles follow the field at a constant phase difference, i.e. they rotate synchronously. Also plotted in Fig. 2 is an exemplary distribution for an unlayered system. Here the synchrony is obviously lost. For more details, we refer the reader to [12].

We now focus on the influence of the simulation methods, i.e. BD versus MD, on the observed dynamic behaviour. To start with, Fig. 3 shows the behaviour of the order parameter ψ at the constant driving frequency $\omega_0^* = 5$ of the field in MD and BD. In both simulation methods, the order parameter increases with the increasing field strength. As just discussed, the layer formation relies on the synchronization of the particles with the field. Hence, the rise of the order parameters is explained by the increasing level of alignment, i.e. synchronization, of the particles with the field. Even though ψ behaves quite similarly in MD and BD at fixed ω_0^*, there are some notable differences. First, ψ rises more steeply in the MD simulations than in the BD ones, implying that layers emerge at smaller field strengths in MD than in BD. According to Fig. 3, the system is layered for $B_0^* \geq 3.5$ in MD, while a field strength of $B_0^* = 5$ is necessary in BD. A further difference is that the order parameter in the MD simulations actually reaches a value

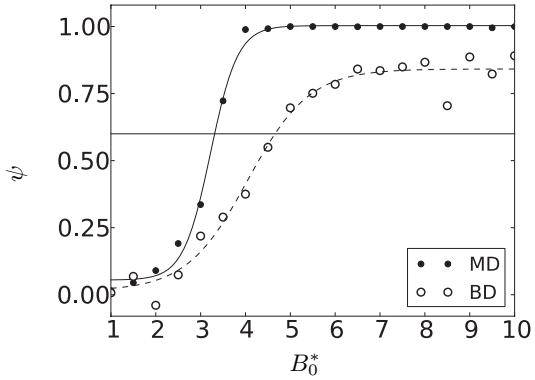


Fig. 3. Behaviour of the order parameter ψ at the constant driving frequency $\omega_0^* = 5$ for MD and BD. The horizontal line indicates where $\psi = 0.6$. Systems with $\psi \geq 0.6$ are considered as layered.

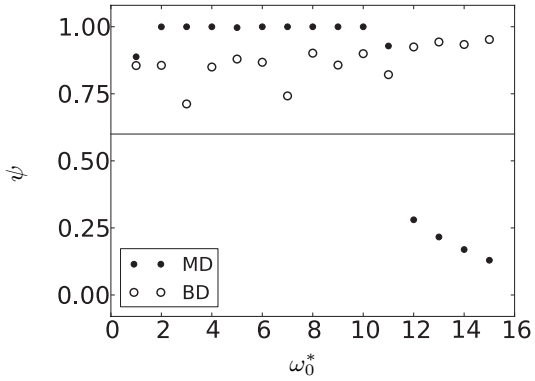


Fig. 4. Behaviour of the order parameter ψ at the constant field strength $B_0^* = 10$ for MD and BD simulations. The horizontal line indicates where $\psi = 0.6$.

of unity, showing that the system ends up in a perfectly layered state. Independent of field strength and frequency, this never happens in BD simulations. Figs. 1*b* and 1*c* illustrate this point. The snapshot from the MD simulations (Fig. 1*b*) shows a system with sharply defined layers, while the BD snapshot shows less well defined ones. These differences can be attributed to the non-conservative random and frictional forces, which appear in the BD equations of motion, but not in the MD ones. In particular, the random forces broaden the layers thereby preventing them from being as well defined as in MD simulations, which keep the order parameter at lower values. The last difference, which is also a manifestation of the random contributions, are the fluctuations in the function ψ that are present in BD, but not in MD. We interpret these fluctuations as a consequence of the fluctuating forces. These perturb the layer structures and particle distributions in between the layers, which results in slightly varying order parameters.

In a next step, we investigate the role of the driving frequency for the layer formation behaviour in MD and BD. To this end, we choose a field strength that is sufficiently high to guarantee the layer formation and synchronization with the field at lower driving frequencies. Fig. 4 shows the order parameter ψ at $B_0^* = 10$ as a function of ω_0^*. The order parameter assumes high values for small frequencies, reflecting the layered nature of the system in both MD and BD. However, ψ drops considerably at $\omega_0^* = 12$ in MD, leaving the system in a non-layered state.

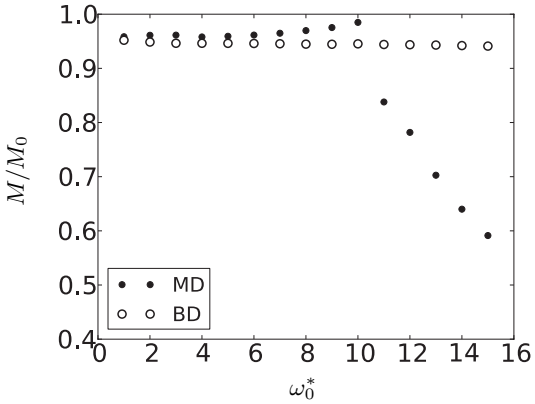


Fig. 5. Time-average of the absolute value of the magnetization M normalized with respect to its saturation value $M_0 = N\mu$.

This behaviour is not mirrored in the BD simulations, where ψ stays above the value that separates the layered from the unlayered regime. To understand the different dynamic behaviour, we note that the two simulation methods differ in the way the system is thermostatted. In MD, the isokinetic thermostat ensures that $T_{\mathrm{rot}} = 1/(2(N-1)) \sum_{i=1}^{N} I\omega_i^2 = 1.35\epsilon/k_B$ is satisfied at all times. This means that if all the particles rotate with the same speed, the maximum rotational frequency admitted by the thermostat is roughly $\omega_0^* \approx 10.4$. Hence, we would expect a drop in the degree of synchronization of the particles beyond this value of the driving frequency. To look into this, we turn to Fig. 5, which depicts the time-averaged absolute value of the magnetization normalized with respect to its saturation value, i.e.

$$\frac{M}{M_0} = \frac{1}{M_0} \left\langle \left| \sum_{i=1}^{N} \boldsymbol{\mu}_i(t) \right| \right\rangle$$

with $M_0 = N\mu$. If M/M_0 is close to unity, the particles are very well aligned with each other and perform a synchronized rotation. Lower values indicate that the particles are less well aligned [12]. Thus, the value of M provides direct insight into the synchronization behaviour of the particles. Fig. 5 shows that M drops significantly between $\omega_0^* = 10$ and 11, confirming that the degree of synchronization does indeed decrease drastically when the driving frequency exceeds $\omega_0^* \approx 10.4$. Consequently, beginning at this value of ω_0^*, an increasing number of particles is not able to follow the field anymore, which ultimately results in the breakdown of layer formation at $\omega_0^* \approx 12$ (cf. Fig. 4). Thus, the strictly imposed temperature in MD prevents the formation of layers after a rotational frequency that typically is considerably smaller than in BD. Indeed, the breakdown of synchronization in BD occurs only at $\omega_0^* \approx 56$ (for $B_0^* = 10$). Moreover, as discussed in detail in [12], the desynchronization in BD is a *frictional* effect rather than a consequence of thermostatting.

Conclusion. In the present paper, we have shown that the layering phenomenon exists in both MD and BD simulations. Due to the absence of non-conservative forces, the minimal field strength required for layer formation is smaller in MD simulations than in corresponding BD simulations. Apart from this difference, the layer formation at a constant angular frequency progresses similarly for both simulation methods.

At a constant driving frequency of the field, however, qualitative differences appear. In MD, the synchronization of the particles with the field, which is imperative for the formation of layers, breaks down at much lower frequencies than in comparable BD simulations. In BD, the breakdown is basically a friction-induced effect [12]. In MD, on the other hand, the thermostat, i.e. the constant temperature, prevents the particles from rotating with adequate speed after a certain driving frequency. In this regime, synchronization of the particles with the field is lost.

Since BD simulations include solvent effects on a single particle, i.e. an approximate level, they may be considered as more realistic for true colloidal suspensions. Nevertheless, the MD simulations are very interesting from a conceptual point of view, since they provide direct insight into the impact of the conservative forces and torques.

To conclude, our analysis shows that the method of thermostatization significantly influences the dynamic behaviour of the particles, and, in consequence, the field-induced formation of layers.

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