Microscale modelling of dielectrophoresis assembly processes

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This work presents a microscale approach for simulating the dielectrophoresis assembly of polarizable particles under an external electric field. The model is shown to capture interesting dynamical and topological features, such as the formation of chains of particles and their incipient aggregation into hierarchical structures. A quantitative characterization in terms of the number and size of these structures is also discussed. This computational model could represent a viable numerical tool to study the mechanical properties of particle-based hierarchical materials and suggest new strategies for enhancing their design and manufacture.

1. Introduction

Electric fields are a handy tool for manipulating micro- and nanomaterials in solutions [1–3]. Dielectrophoresis (DEP), i.e. the motion of polarizable objects in a non-uniform electric field, has become a vastly used technique...
to separate, sort, and trap systems such as cells [4,5], nano- and microparticles [6] and biomolecules [2], to name but a few.

A remarkable feature of DEP is that it can be used to drive the assembly of significantly small materials, such as nano-colloids, thus providing, for instance, an efficient strategy to deposit dielectric and metallic nanoparticles onto electrode arrays and to control their arrangement [7,8]. If coated with polymers, such systems can exhibit a hierarchical structure, like pearl chains aligned along the field lines [9] or well-defined networks made of a percolating mesh of particle-rich walls surrounding particle-free ‘voids’ [10,11].

The ability to assemble hierarchical structures starting from micro- or nano-particles responsive to an electric field is crucial in several technological applications of modern industry, ranging from medical diagnostics and photolithography up to material science for the design of soft composites with high tunable porosity [12–17]. Indeed, the hierarchical DEP process may provide a highly desirable mechanism to realize large-scale ordered materials, built from a field-directed assembly mechanism dominating the Brownian motion of particles [18].

Previous simulations, including dipolar and van der Waals interactions among spherical particles, have found several variants of structures (linear aggregates, droplets, columns) resulting from the phase separation into regions of a high and low density of colloidal particles [19,20].

Here we present a numerical scheme aimed at describing the assembly process of nanoparticles capable of forming instantaneous dipoles under the effect of the surrounding electric field. The model is based on a classical version of Drude oscillators [21], in which a polarizable particle is described in terms of a core-Drude pair acquiring an induced dipole moment in the presence of an applied electric field and whose evolution is governed by a couple of Langevin equations (one for the Drude and the other one for the core particle (CP)) integrated by LAMMPS [22]. With respect to previous models only considering dispersed dielectric particles, this one allows for controlling the dynamics of the polarization process as well as a number of dynamic features of the colloids, such as friction and noise-induced effects. In addition, such an approach would be suitable for simulating multiscale effects occurring with polarizable particles dispersed in a mesoscopic solvent, which could be modelled using, for example, the lattice Boltzmann method [23].

Our computational model is found to capture key features of the assembly process, such as the early dynamics characterized by the generation of chains of colloids and their clustering into hierarchical structures by forming crossing points among the chains.

The paper is organized as follows. In §2, we describe the computational model of the polarized particle, and in §3, we report our numerical results. In particular, we show the early and late time evolution of the assembly process and a cluster analysis which quantitatively captures their formation.

2. Computational model

To shed light on the basic mechanisms driving the formation of assembled and ordered structures of nanoparticles, we have run numerical simulations neglecting hydrodynamic interactions and considering only steric interactions, Brownian motion and explicit many-body effects induced by the presence of an external electric field.

More precisely, the polarizability $\alpha$ of a particle with a charge $q$ is modelled by introducing a mobile Drude particle (DP) having charge $q_D$ bound by a harmonic potential with elastic constant $k_D$ (assumed the same for all bonds) to a CP with charge $q_C = q - q_D$ (figure 1). This sets the net charge of the system core-DP to $q$ [21], in the following assumed equal to zero (neutral charge). In the absence of an electric field, the DP oscillates around the equilibrium position $r_C = 0$ of the CP in the centre of mass frame of the core-Drude two-particle system. Since we assume $m_D \ll m_C$, the centre of mass essentially corresponds to the centre of the CP. Hence, the couple core-Drude has a net charge $q$ with average dipole moment $\mu = 0$. If a uniform electric field $E$ is applied, the Drude
unpolarized particle, \( m = 0 \)

applied electric field, \( E \)

displacement, \( d = q_D E / K_D \)

polarized particle, \( m = q_D^2 E / K_D \)

Figure 1. The cartoon shows the core-Drude particle model. In the absence of external electric field \( E \), the dipole moment is \( \mu = 0 \). Here the core charge is positive the Drude one is negative, with \( q_C = -q_D \). Once an electric field is applied, a spring-like force opposes to the field and the dipole moment \( \mu = q_D^2 E / K_D \) is set. (Online version in colour.)

is displaced at distance \( d = q_D E / K_D \) (with \( q_D < 0 \)) in the centre of mass frame, and the average dipole moment is \( \mu = q_D^2 E / K_D \). Thus one gets \( \alpha = q_D^2 / k_D \) [21,24].

In the external reference frame and neglecting \( r_C = 0 \), the time evolution of each Drude and CP is governed by two Langevin equations, respectively:

\[
m_C \frac{d^2 r_{C,i}}{dt^2} = -\gamma_C \frac{dr_{C,i}}{dt} - \frac{\partial U}{\partial r_{C,i}} + \sqrt{2 k_B T \gamma_C} \xi_i(t) + q_C E \tag{2.1}
\]

and

\[
m_D \frac{d^2 r_{D,i}}{dt^2} = -\gamma_D \frac{dr_{D,i}}{dt} - \frac{\partial U}{\partial r_{D,i}} + \sqrt{2 k_B T \gamma_D} \xi_i(t) + q_D E \tag{2.2}
\]

where \( r_{C,i} \) and \( r_{D,i} \) are the positions of the \( i \)-th core and DPs, \( \gamma_C \) and \( \gamma_D \) are the viscous friction felt by each of them, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \xi_i \) is an uncorrelated Gaussian noise with zero mean and unit variance, \( m_C \) and \( m_D \) (with \( m_D \ll m_C \)) are the masses of the Drude and the CPs and \( E \) is an external electric field. Finally, \( U \) represents the total potential given by the sum of three terms \( U = U_{\text{bond}} + U_{\text{elec}} + U_{WCA} \). The first one is the core-Drude harmonic potential

\[
U_{\text{bond}} = \sum_i \frac{1}{2} k_D |r_{C,i} - r_{D,i}|^2 \tag{2.3}
\]

the second one represents the Coulomb interactions

\[
U_{\text{elec}} = \sum_i \sum_{j>i} \frac{q_i q_j}{|r_i - r_j|} \tag{2.4}
\]
and the third one is a Weeks–Chandler–Andersen (WCA) potential accounting for the interparticle repulsion given by

\[
U_{WCA} = \begin{cases} 
4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \frac{(\sigma/2)^6}{r^6} & \text{if } r < 2^{1/6} \sigma \\
0 & \text{if } r \geq 2^{1/6} \sigma.
\end{cases}
\]  

Here \( \epsilon \) defines the energy scale, \( r \) is the centre-to-centre separation between Drude and CPs, and \( \sigma \) is the value of \( r \) at which \( U_{WCA} = 0 \) which is, to a good approximation, the diameter of the CP.

It is worth highlighting that the internal Coulomb interaction between the bonded core and DPs is not accounted for in the model [21,24].

3. Numerical results

We have considered a dilute suspension of 322 colloidal particles of diameter equal to 10 nm, dispersed in a periodic cubic box of size 3000 \( \times \) 3000 \( \times \) 3000 nm\(^3\). This sets a particle volume fraction of approximately \( 4 \times 10^{-4} \). To capture the dynamic behaviour at late times, our simulations are run for \( 6 \times 10^9 \) timesteps \( \Delta t \), where \( \Delta t = 2 \times 10^{-12} \) s. This corresponds to a total real-time of 12 milliseconds, which is necessary to catch an almost complete dynamics of the aggregation process. Particle positions are randomly initialized by a uniform distribution with velocities extracted from the Maxwell distribution at a temperature equal to 300 K. We have also set \( \alpha = 3.8 \times 10^{-32} \) m\(^2\) V\(^{-1}\) [18], \( m_D/m_C \simeq 1/30 \), \( \gamma_C = 800 \times 10^{-9} \) s and \( \gamma_D = 4 \times 10^{-9} \) s. It is also worth highlighting that the high polarizability \( \alpha \) of each colloid is due to the interaction among the colloid itself and the surrounding solvation shell, comprised within a distance of about 10 nm [18]. Thus, each colloid is modelled including its respective solvation shell, thus yielding to a spherical object of radius 20 nm (the colloidal radius plus the depth of the solvation shell).

We initially discuss the dynamics of the assembly process occurring in the presence of an oscillating electric field \( \mathbf{E} = E_0 \cos(\omega t) \mathbf{u}_z \) (where \( \mathbf{u}_z \) is a unit vector parallel to the \( z \)-direction and \( \omega \) is the angular frequency), of amplitude \( E_0 = 0.020 \) kV mm\(^{-1}\) and frequency \( \nu = \omega/2\pi = 500 \) kHz, applied along the \( z \)-axis. Such values are comparable with the experimental ones reported in [10,11].

In figure 2, a typical early-time evolution of the assembly process is shown. Once the field is switched on, the core-DPs acquire a dipole moment whose orientation fluctuates due to the combined effect of Brownian motion and oscillating electric field (figure 2, \( t = 0.1 \) ms). Such dynamics favours the approach of a pair of particles which join together due to the attractive Coulomb potential among negatively and positively charged regions (figure 2, \( t = 1 \) ms). This stage is followed by a further one in which such couples, when they come close to another particle, assemble and give rise to monodimensional colloidal chains, whose length increases over time (figure 2, \( t = 2 \) ms and \( t = 4 \) ms).

The generation of anisotropic chains of colloids resulting from the assembly of polarizable nanoparticles represents the first necessary step preceding a more complex topological arrangement, i.e. the formation of crossing points among chains. This process (whose time evolution is shown in figure 3) occurs when colloidal aggregates with different orientations of \( \mathbf{\mu} \) approach and join together, giving rise to fully three-dimensional larger clusters (see figure 3, at \( t = 6 \) ms and \( t = 8 \) ms). Concurrently, the assembly of particles into long chains proceeds and more complex structures, such as three- and fourfold aggregates, are produced (see figure 3 at \( t = 10 \) ms and \( t = 11 \) ms), thus increasing the cluster size while diminishing their number.

The addition of a static electric field \( \mathbf{E}_{os} = E_{os} \mathbf{u}_z \) of magnitude \( E_{os} = 0.02 \) kV mm\(^{-1}\) and applied along the \( z \)-direction, moderately affects the dynamic behaviour (figure 4). Indeed, while at early times colloidal aggregates look isotropically distributed within the box (\( t = 1 \) ms), subsequently (from \( t = 4 \) ms to \( t = 8 \) ms) long chains progressively align along the direction imposed by the field and at late times (\( t = 8 \) ms) they essentially exhibit a common orientation (\( t = 11 \) ms).
Figure 2. The figure shows the time evolution, up to 4 ms, of the assembly process of nano-particles in the presence of an oscillating electric field. Once the field is switched on, the particles, initially randomly distributed ($t = 0.1$ ms), gradually approach and assemble into chains ($t = 1$ ms and $t = 2$ ms), whose number increases at late times ($t = 4$ ms). Green vectors indicate the direction of the induced dipole moment. The largest aggregate of colloids is shown in red. (Online version in colour.)

Figure 3. The figure shows the incipient formation, occurring from 6 ms to 11 ms, of crossing points among clusters of polarized nanoparticles in the presence of an oscillating electric field. Note that clusters are in average oriented randomly in the simulation box. The vectors indicate the direction of the induced dipole moment. The largest aggregate is shown in red. (Online version in colour.)
Figure 4. The figure shows the time evolution, up to 11 ms, of the assembly process of nano-particles in the presence of both an oscillating and a static electric field oriented along the z-axis. Unlike the case shown in figure 3 here, at late times, clusters have a common average alignment parallel to that axis. Green vectors indicate the direction of the induced dipole moment. The largest cluster is shown in red. (Online version in colour.)

A quantitative evaluation of the cluster dynamics is obtained by the deep first search (DFS) method [25], which can identify all colloidal particles belonging to the same cluster by using methods of the graph theory [26], even in the case in which such particles are not directly connected. Assuming two colloids to be in direct connection whenever the mutual distance is below 50 nm, the cluster analysis of the dynamics shown in figure 3 and in figure 4 is reported in figure 5. In both cases, the number of clusters $N_{cl}$, starting from $N_{cl} = 322$ single colloidal particles, diminishes over time (figure 5a) due to colloidal aggregation, although the presence of a sufficiently intense static electric field favours a faster decrease. This occurs basically because clusters are forced to orient preferentially along one axis (the z-axis), thus having less chance to turn around and catch other neighbouring aggregates. The curves are found to follow a stretched exponential behaviour $f(t) = a e^{-t/b^c}$ where $c$ is around 0.7 (figure 5b), a behaviour probably due to memory effects induced by the electric field in systems made of charged colloids, very likely absent with uncharged particles. We note that such results are rather robust since, for lower values of the mutual distance (such as 40 nm) between two colloids, the plots remain essentially unaltered.

Alongside the decrease of $N_{cl}$, the size of the clusters augments over time. This is shown in figure 5c where the time evolution of the size $S_{max}$ of the largest cluster is plotted. Here $S_{max} = \max_{n_p \in C_i} \{n_p\}$, where $n_p$ is the number of particles assembled in the $i$-th cluster $C_i$. This quantity, starting from $S_{max} = 1$ (i.e. a cluster made of a single particle), is found to increase less rapidly once a static electric field is applied, a result overall expected since, as previously mentioned, the capture of nearby colloids is a less likely event. Here the time behaviour is well fitted by a power law $t^k$ (valid for a limited period of time), with $k \approx 0.45$ and $\approx 0.64$ obtained with and without the static electric field, respectively. The average size of the clusters increases over time as well (figure 5d) although, in the presence of a the static electric field, such growth is slightly favoured. This occurs likely because, in that case, the size of the largest cluster is smaller than the one obtained with the sole oscillating field. Hence, smaller clusters can capture more particles, thus increasing the value of $\langle S_{cl} \rangle$. 
Figure 5. (a) Time evolution of number of clusters $N_{cl}$ in the presence of an oscillating electric field (red/plusses) and with an additional static field (green/crosses). In both cases, the plots can be best fitted with a stretched exponential $f(t) = ae^{-t/b^c}$ where $a \approx 337, b \approx 7, c \approx 0.72$ for the red/plusse plot, and $a \approx 348, b \approx 6, c \approx 0.66$ for green/crosses one. The plot shows the linearized curves, while the dotted line represents a guide for the eye with slope approximately 0.7. (c) Time evolution of size $S_{cl}$ of the largest cluster of particles. Dashed lines fit the curves with a power law $g(t) = ht^k$, with $h \approx 4.6, k \approx 0.63$ dashed black line, and $h \approx 4.6, k \approx 0.45$ dashed blue line. (d) Time evolution of the average clusters size $\langle S_{cl} \rangle$. Bars represent the standard deviation. In the presence of the static field $\langle S_{cl} \rangle$ grows slightly faster. (Online version in colour.)

Figure 6. Normalized probability density function of the number of clusters $N_{cl}$ at increasing times in the presence of an oscillating field (a) and of an oscillating plus a static field (b). (Online version in colour.)

Finally, the cluster dynamics can be also quantified by looking at the time evolution of the normalized probability density function (pdf) of $N_{cl}$ without and in the presence of a static electric field (figure 6a,b). Indeed they display a rather similar behaviour characterized by a transition
from an early-time highly localized distribution towards a broad-shaped one at late times, when $N_{cl}$ exhibits a slightly more uniform structure.

4. Conclusion and outlook

To summarize, we have presented a computational scheme for simulating the process of DEP assembly of polarizable particles driven by an external electric field. Particles are modelled by means of a classical version of the core-Drude theory, in which their dynamics is governed by a Langevin equation.

The model is found to capture key aspects of the assembly process observed experimentally, such as the formation of chain-like aggregates of colloids and the crossing points among different chains. These clusters are the building blocks necessary to achieve more complex arrangements, such as the hierarchical cellular scaffolds described in [10,11].

In particular, our simulations show that an oscillating electric field drives the growth of large colloidal clusters, whose number decreases over time following a stretched exponential behaviour while the maximum size augments essentially following a power law behaviour. The addition of a static electric field with a magnitude akin to the oscillating one, other than favouring a global orientational order of the clusters along the field, produces only a mild effect on the dynamics, slightly hindering the process of colloidal aggregation. Our results, besides shedding light on the physical mechanisms sustaining the cluster formation, represent a first step towards the modelling of higher complex hierarchical arrangements, potentially observed at larger particle volume fraction.

Further developments of this model will aim at simulating DEP assembly in the presence of hydrodynamic interactions, in order to capture the multiscale physics ranging from particle size level ($\sim$ tens of nanometres) to the typical colloidal domain dimension ($\sim$ tens of micrometres) [27, 28].

**Data accessibility.** Supporting data are available via Dryad: https://doi.org/10.5061/dryad.5mkkwh75m.

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**Competing interests.** We declare we have no competing interests.

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