Self-assembly and alignment of anisotropic colloidal particles are important processes that can be influenced by external electric fields. However, dielectric nanoparticles are generally hard to align this way because of their small size and low polarizability. In this work, we employ the coupled dipole method to show that the minimum size parameter for which a particle may be aligned using an external electric field depends on the dimension ratio that defines the exact shape of the particle. We show, for rods, platelets, bowls, and dumbbells, that the optimal dimension ratio (the dimension ratio for which the size parameter that first allows alignment is minimal) depends on a nontrivial competition between particle bulkiness and anisotropy because more bulkiness implies more polarizable substance and thus higher polarizability, while more anisotropy implies a larger (relative) difference in polarizability. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3701615]
that \( \alpha_c \) is diagonal. Furthermore, the particles considered here have at least a four-fold rotational symmetry around one axis, here defined as their Cartesian \( z \)-axis, which results in \( \alpha_c \) having the property that \( \alpha_{xx} = \alpha_{yy} \). The anisotropy of the cluster polarizability is therefore completely characterized by \( \alpha_{zz} - \alpha_{xx} \).

Within the theoretical framework of the CDM, the dipole couplings are the sole cause of the anisotropy of the cluster polarizability (where \( \alpha_{zz} \neq \alpha_{xx} \)). This can be seen by noting that one atom is considered to have an isotropic polarizability, \( \alpha_0 \mathbf{l} \), and, thus, a cluster of \( N \) of these atoms would, if atom-atom interactions were ignored, have an isotropic polarizability \( N \alpha_0 \mathbf{l} \). Hence, the magnitude of the polarization of the cluster would be independent of the orientation of the external electric field \( \mathbf{E}_0 \). In contrast, in the CDM, where many-body effects are included in the calculation, the (diagonalized) cluster polarizability in general does not have equal entries on the diagonal and thus has an orientation-dependent polarizability.

An electric field \( \mathbf{E}_0 \) applied to a cluster with polarizability \( \alpha_c \) will induce a polarization and thus lower the particle’s electrostatic (potential) energy to \(^{32}\)

\[
V_E = -\frac{1}{2} \mathbf{E}_0 \cdot \alpha_c \cdot \mathbf{E}_0 = -\Delta \cos^2 \theta + \text{constant},
\]

where \( \theta \) represents the angle between the rotational symmetry axis of the particle and \( \mathbf{E}_0 \), and where

\[
\Delta = \frac{1}{2} (\alpha_{zz} - \alpha_{xx}) \mathbf{E}_0^2 \equiv \frac{1}{2} \Delta_f \mathbf{N} \alpha_0 \mathbf{E}_0^2,
\]

with

\[
\Delta_f \equiv (\alpha_{zz} - \alpha_{xx}) / N \alpha_0.
\]

We note that \( \Delta_f \) is the difference \( f_{zz} - f_{xx} \) of the diagonal elements of the so-called \((3 \times 3)\) enhancement factor \( f_c \equiv \alpha_c / N \alpha_0 \), which is a measure for how much the interactions between the point dipoles enhance or reduce the polarizability. Our numerical calculations\(^{32}\) suggest that \( \Delta_f \) is essentially independent of \( N \) and, thus, depends only on the particle’s shape and on \( \bar{a} \) but not on its overall size. This independence is approximate, since for small values of \( N \), effects of the discretization employed by the CDM become appreciable. However, for the values of \( N \) that we employ, approximations for \( f_c \) and \( \Delta_f \) are very accurate, which is illustrated by the excellent agreement between values calculated using the CDM\(^ {32}\) and those calculated using continuum theory.\(^ {35-39}\)

The angular distribution function \( \psi(\theta) \) of a particle in solution, subject to an electric field \( \mathbf{E}_0 \) and to Brownian motion due to the molecular medium at temperature \( T \), is proportional to the Boltzmann factor,

\[
\psi(\theta) = \frac{\exp(\beta \Delta \cos^2 \theta)}{4\pi \int_0^{\pi/2} \sin \theta \, d\theta \exp(\beta \Delta \cos^2 \theta)},
\]

where \( \beta = 1/k_B T \) is the inverse of the thermal energy. We can quantify the degree of orientational order of this particle by introducing the nematic order parameter

\[
S(\beta \Delta) = \langle P_2(\cos \theta) \rangle = 4\pi \int_0^{\pi/2} \sin \theta \psi(\theta) P_2(\cos \theta) \, d\theta,
\]

where \( P_2(\cdot) \) is the second Legendre polynomial and \( \langle \cdot \rangle \) denotes the ensemble average. The distribution \( \psi(\theta) \) for several values of \( \Delta \), and the order parameter \( S(\beta \Delta) \), are plotted in Fig. 1.

From Fig. 1, it is clear that an externally applied electric field will only align a particle substantially if \( \Delta \gtrsim k_B T \). The number of atoms \( N^* \) in the cluster for which \( \Delta \approx k_B T \) is, via Eq. (2), given by

\[
N^* = \frac{2k_B T}{\Delta_f \alpha_0 E_0^2}. \tag{3}
\]

For given \( \bar{a} \), we can calculate \( N^* \) numerically by using the value of \( \Delta_f \) as calculated within the CDM for (relatively) small clusters (with \( N \approx 10^4 \)). This is accurate since, as noted before, \( \Delta_f \) is essentially independent of \( N \).

The shape of an \( l \times l \times L \) cuboid is determined by its shape parameter \( r \equiv l/L \). For each \( r \), we can calculate \( N^* \) [by making use of Eq. (3)] and, hence, the size parameter for which the cuboid satisfies \( \Delta = k_B T \). This “size parameter” is, throughout this work, defined as the length of the particle when measured along the electric field if the particle is perfectly lined up.\(^ {40}\) For rods, this is given by \( aL^* \) and for platelets by \( al^* \), where \( L^* \) and \( l^* \) can be calculated from \( r \) and \( N^* \) by

\[
L^* = \left( \frac{N^*}{r^2} \right)^{1/3}, \quad l^* = \left( N^* r \right)^{1/3}, \tag{4}
\]

and \( a \) follows from \( a = \bar{a} \alpha_r^{1/3} \).

From our numerical data we find that \( \Delta_f \) is largest for very anisotropic particles.\(^ {32}\) This implies, via Eq. (3), that \( N^* \) is smallest for very anisotropic particles. However, when converting this \( N^* \) to a length such as \( L^* \) or \( l^* \), a competing mechanism arises from the fact that more anisotropy means less bulkiness. For rods, we note that lowering \( r \) has two effects: on the one hand, it lowers \( N^* \) because more anisotropy enhances \( \Delta_f \); on the other hand, it increases \( L^* \) via Eq. (4). Similarly, for platelets, higher anisotropy is achieved through raising \( r \), while \( l^* \) rises with increasing \( r \) (see Eq. (4)). In other words, less atoms “fit” in a highly anisotropic particle for a given \( L^* \) (for rods) or \( l^* \) (for platelets).
The length $a L^*_0$ (a) and the width $a l^*$ (b) for which $l \times l \times L$ cuboidal rods and platelets, respectively, first become alignable by an electric field $E_0 = 100$V/mm$^{-1}$, as a function of their shape ($llL$ and $lll$, respectively), for several different lattice constants $a = a/\alpha = 1.75, 2, 2.5$ and $3$. The temperature is $T = 293$K, and the atomic polarizability is $\alpha_0 = 5.25$ Å$^3$. The dots denote the minima in the graphs.

In Fig. 2 we plot $L^*$ (for rods) and $l^*$ (for platelets) as a function of the shape parameter $r = l/L$ (for rods) and $r^{-1} = L/l$ (for platelets), for several values of the lattice constant. The other parameters are the experimentally typical values of $T = 293$K, $E_0 = 100$V/mm$^{-1}$ and $\alpha_0 = 5.25$ Å$^3$. For rods, we find a minimum $L^*$ around $l/L \approx 0.62$; this dimension ratio thus defines the optimum shape for alignment of rods in an external electric field. For platelets, a minimum $l^*$ is observed at $L/l \approx 0.38$. The locations of these minima do not depend strongly on the lattice constant. Additional numerical calculations, not shown here, confirm that this (approximate) independence also holds for $\tilde{a} > 3.0$. As could be expected, however, a lower lattice constant does imply a lower $L^*$ or $l^*$.

The same analysis can be applied to clusters of other shapes. Here, we show results for bowl-shaped and dumbbell-shaped particles. The bowl shape is achieved by revolving a crescent around its symmetry axis. The construction of this crescent shape is depicted and discussed in Fig. 3. Note that bowls with $dl/\sigma = 0$ are hemispherical shells and bowls with $dl/\sigma > 0$ are hemispheres. For $dl/\sigma > 0.5$, instead of a bowl in the conventional meaning, we get a hemisphere with a protrusion on its flat side (the green area in Fig. 3). “Bowls” with $dl/\sigma = 1$ are spheres. The dumbbell shape is a simpler design: we take two spheres of diameter $\sigma$ at center-to-center distance $L$ from each other and take as the shape of the dumbbell the region in which all points are either in one sphere or in the other, or in both. Thus, $L/\sigma = 0$ corresponds to a sphere, $L/\sigma = 1$ corresponds to two touching spheres and $L/\sigma > 1$ refers to two separate spheres. Once the shape is determined we intersect it with a simple cubic lattice grid with spacing $a$, resulting in a cluster of atoms of approximately the appropriate shape. Note that the size parameter, using the definition mentioned earlier, is given by $\sigma$ for bowls, and $\sigma + L$ for dumbbells.

As in the case of rods and platelets, extrapolation (Eq. 3) has to be used to determine the atom number $N^*$ for which $\Delta \gtrsim k_B T$. Furthermore, since we no longer have a straightforward relation to determine the size parameter ($\sigma^*$ or $\sigma^* + L^*$) from a given $N^*$, we use extrapolation of the phenomenological dependence of $N$ on $\sigma (N \propto \sigma^3)$ to estimate $\sigma^*$. For dumbbells, we subsequently add $L^*$ (which can be calculated from $L/\sigma$ and $\sigma^*$) to gain the correct size parameter. The result is plotted in Fig. 4.

For bowls (Fig. 4(a)), we observe that the optimal shape is located around $dl/\sigma \approx 0.52$, (corresponding to a slightly protruded hemisphere). Note that for $dl/\sigma > 0.5$, the bowl shape construction used in this work no longer produces a bowl in the traditional sense of the word. Hence, the optimally alignable “traditional” bowl is as bulky as possible: a hemisphere.

For dumbbells (Fig. 4(b)), the minima lie around $L/\sigma \approx 0.51$. Thus, like in the case of rods, the optimum size ratio for dumbbells lies in-between the maximally anisotropic and bulky configuration (two touching spheres and one sphere, respectively).

In conclusion, we showed that the dependence of the minimum size of an alignable particle on the shape ratio of the particle is nontrivial, as it is not in general true that for alignment, the more anisotropic the particle the better, nor are bulkier particles always better: for all the particle shapes studied here, the optimum shape lies in-between. We note here that for lower values of $\tilde{a}$ (strong coupling), the graphs of Figs. 2 and 4 are very flat, such that a broad range of dimension ratios can be considered near-optimal. Interestingly, the
polarizability is a function of their shape parameters \( \sigma \) and \( L \), respectively. Here, \( d \) is the thickness of a bowl and \( L \) is the separation of the two composing spheres of a dumbbell. The bowls and dumbbells are built up of atoms on a simple cubic lattice with dimensionless lattice spacings \( a \) to \( 1/3 \), 2, 2.5, and 3. The temperature is \( T = 293K \), and the atomic polarizability is \( a_0 = 5.25 \AA^3 \). The dots denote the minima in the graphs.

This work is part of the research programme of FOM, which is financially supported by NWO. Financial support by an NWO-VICI grant is acknowledged.