Communication: Bulkiness versus anisotropy: The optimal shape of polarizable Brownian nanoparticles for alignment in electric fields

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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]

Self-assembly of nanoparticles is an interesting thermodynamic process in which particles spontaneously form highly ordered structures with important technical applications in new materials and devices. In recent years, the technology of synthesizing anisotropic nanoparticles has made tremendous progress,[1,2] and has resulted in the synthesis and analysis of colloidal rods,[3] bowls[4–7] and dumbbells.[8] Anisotropic particles are known to self-assemble into orientationally (and possibly positionally) ordered structures under the influence of their interparticle interactions.[9–16] However, this process is often difficult to achieve in practice and hampered by slow dynamics. Several techniques can be employed to assist the self-assembly process, such as alignment of the particles by introducing a substrate to the system,[17,18] employing a fluid flow,[19] or applying external magnetic[20] or electric[21–24] fields. The reason an external electric field can align an anisotropic particle is due to its anisotropic polarizability, which causes the particle's potential energy to vary with its orientation in the field. Since the thermal Brownian motion competes with the tendency to align, the potential energy difference has to be high enough in order to overcome these fluctuations and substantially align the particle. For nanoparticles, this is hard to achieve: because of their small size, they are generally only slightly polarizable and thus the difference in potential energy will, for accessible electric fields, be low. In this work, we investigate the conditions for alignment, and we show that the minimum size to align a particle depends on the shape of the particle because of a nontrivial competition between particle bulkiness and anisotropy.

The calculations in this work are based on the coupled dipole method (CDM).[25–32] In the CDM, we model a particle as a cluster of N coupled point dipoles at fixed positions. Each dipole $\mathbf{p}_i$ ($i = 1, \ldots, N$) can be polarized due to a local electric field $\mathbf{E}_{\mathrm{loc}}^{(i)}$ such that $\mathbf{p}_i = \alpha_0 \mathbf{E}_{\mathrm{loc}}^{(i)}$, where α_0 is the (scalar)

polarizability of the dipole.[33,34] The dipoles are purely induced, i.e., they are assumed to have no permanent moment. The local field $\mathbf{E}_{\mathrm{loc}}^{(i)}$ at the site of dipole i consists of an externally applied field $\mathbf{E}_0$ and the (nonretarded) field due to the other $N - 1$ polarized dipoles. All many-body effects that arise in this way are accounted for by the CDM without the use of approximations.

Physically, the point dipoles could represent "chunks" of polarizable matter in general, but here we think of individual polarizable atoms or molecules, with α_0 in the cubic Angstrom regime. In this work, we only consider dipoles on a cubic lattice with lattice spacing a. We can then approximate the atomic polarizability by the Clausius-Mossotti relation

$$\alpha_0 \approx \frac{3a^3 \epsilon_m}{4\pi} \frac{\epsilon_p/\epsilon_m - 1}{\epsilon_p/\epsilon_m + 2},$$

where ϵ_p is the dielectric constant of the substance that the atoms represent, and ϵ_m is the dielectric constant of the solvent that the cluster is dispersed in. From this relation, as well as from the theory of the CDM,[32] it can be seen that the dipole-dipole coupling is fully characterized by the dimensionless lattice spacing $\tilde{a} \equiv a/\alpha_0^{1/3}$. For typical ratios of ϵ_p/ϵ_m, $\tilde{a}$ is of order unity; in this work we only consider $\tilde{a} \gtrsim 1.7$ to prevent the polarization catastrophe.[31,34]

The 3×3 polarizability matrix $\boldsymbol{\alpha}_c$ of the whole cluster of N particles is defined by

$$\sum_{i=1}^{N} \mathbf{p}_i = \boldsymbol{\alpha}_c \cdot \mathbf{E}_0,$$

and can be calculated by (large-)matrix manipulation for a given cluster composed of up to $N \approx 10^{5 \pm 1}$ dipoles.[27,30,32] One can show that $\boldsymbol{\alpha}_c$ is symmetric if all dipoles have the same polarizability α_0 and, as a consequence, $\boldsymbol{\alpha}_c$ is diagonal in an appropriate Cartesian coordinate frame. In this work, we will always choose the Cartesian axes such

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that $\boldsymbol{\alpha}_c$ 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 $\boldsymbol{\alpha}_c$ 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, $\alpha_0 \mathbf{I}$, and, thus, a cluster of N of these atoms would, if atom-atom interactions were ignored, have an isotropic polarizability $N\alpha_0 \mathbf{I}$. 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 $\boldsymbol{\alpha}_c$ will induce a polarization and thus lower the particle's electrostatic (potential) energy to[32]

$$V_E = -\frac{1}{2}\mathbf{E}_0 \cdot \boldsymbol{\alpha}_c \cdot \mathbf{E}_0 = -\Delta \cos^2\theta + \text{constant}, \quad (1)$$

where θ represents the angle between the rotational symmetry axis of the particle and $\mathbf{E}_0$, and where

$$\Delta = \frac{1}{2}(\alpha_{zz} - \alpha_{xx})\mathbf{E}_0^2 \equiv \frac{1}{2}\Delta_f N\alpha_0 E_0^2, \quad (2)$$

with

$$\Delta_f \equiv \frac{(\alpha_{zz} - \alpha_{xx})}{N\alpha_0}.$$

We note that Δ_f is the difference $f_{zz} - f_{xx}$ of the diagonal elements of the so-called (3 × 3) enhancement factor $\mathbf{f}_c \equiv \boldsymbol{\alpha}_c/N\alpha_0$, which is a measure for how much the interactions between the point dipoles enhance or reduce the polarizability. Our numerical calculations[32] suggest that Δ_f is essentially independent of N and, thus, depends only on the particle's shape and on $\tilde{a}$ 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 $\mathbf{f}_c$ and Δ_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,

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

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

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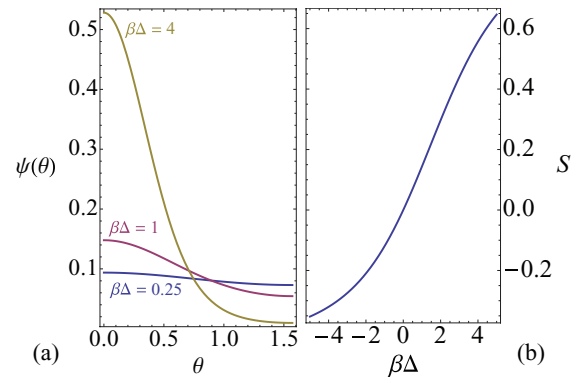

FIG. 1. The angular distribution function $\psi(\theta)$ (a), and the order parameter S (b), of an anisotropic particle with orientational energy $V_E(\theta) = -\Delta\cos^2\theta$ in an external electric field $\mathbf{E}_0$. Here, θ is the angle between the particle's rotational symmetry axis and $\mathbf{E}_0$ and Δ is the energy difference of turning the particle from its least to its most favorable orientation.

where P_2 is the second Legendre polynomial and $\langle . \rangle$ denotes the ensemble average. The distribution $\psi(\theta)$ for several values of Δ, 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 $\Delta \gtrsim k_BT$. The number of atoms N* in the cluster for which $\Delta \approx k_BT$ is, via Eq. (2), given by

$$N^* = \frac{2k_BT}{\Delta_f \alpha_0 E_0^2}. \quad (3)$$

For given $\tilde{a}$, we can calculate N* numerically by using the value of Δ_f as calculated within the CDM for (relatively) small clusters (with $N \approx 10^4$). This is accurate since, as noted before, Δ_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 $\Delta = k_BT$. 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

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

and a follows from $a = \tilde{a}\alpha_0^{1/3}$.

From our numerical data we find that Δ_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 Δ_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).
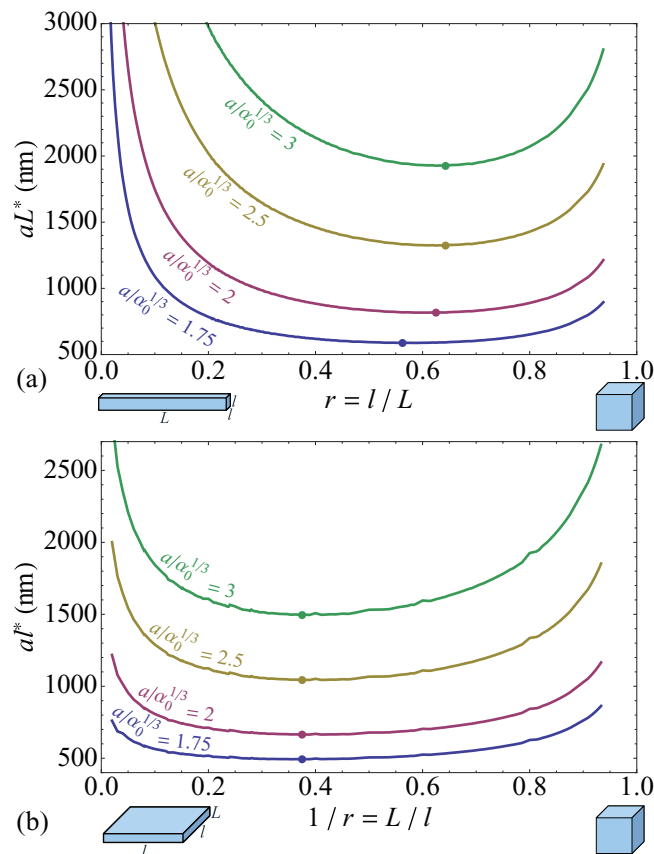
FIG. 3. To get the bowl shape, we revolve a crescent around its symmetry axis.[4] This crescent is the result of the set-theoretic subtraction of a disk with diameter $\sigma' > \sigma$ from a disk with diameter σ. The relative position of the two disks and the diameter σ' have to be chosen such that the center of the small disk lies on the line connecting the two points where the edges of the disks intersect, and such that in its middle, the thickness of the crescent is d. In this work, we also allow $d > \sigma/2$, which we associate with the set-theoretic intersection of the two disks (the green area with thickness d').

FIG. 2. The length aL^* (a) and the width al^* (b) for which $l \times l \times L$ cuboidal rods and platelets, respectively, first become alignable by an electric field $E_0 = 100\,\text{Vmm}^{-1}$, as a function of their shape (l/L and L/l, respectively), for several different lattice constants $\tilde{a} = a/\alpha_0^{1/3} = 1.75$, 2, 2.5 and 3. The temperature is $T = 293\,\text{K}$, and the atomic polarizability is $\alpha_0 = 5.25\,\text{Å}^3$. 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 $T = 293\,\text{K}$, $E_0 = 100\,\text{Vmm}^{-1}$ and $\alpha_0 = 5.25\,\text{Å}^3$. 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,[41] 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.[4] The construction of this crescent shape is depicted and discussed in Fig. 3. Note that bowls with $d/\sigma = 0$ are hemispherical shells and bowls with $d/\sigma = 0.5$ are hemispheres. For $d/\sigma > 0.5$, 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 $d/\sigma = 1$ are spheres. The dumbbell shape is a simpler design: we take two spheres of diameter σ at center-to-center distance L from each other and take as the shape of the dumbbell the
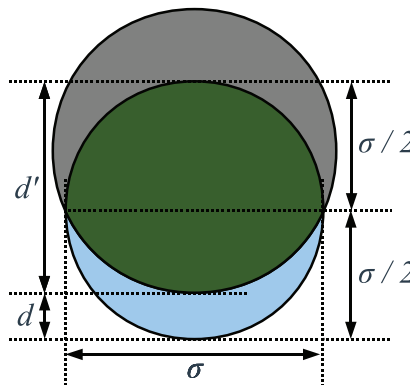
region in which all points are either in one sphere or in the other, or in both. Thus, $L/\sigma = 0$ corresponds to a sphere, $L/\sigma = 1$ corresponds to two touching spheres and $L/\sigma > 1$ refers to two separate spheres. Once the shape is determined we intersect it with a simple cubic lattice 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 σ 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 (σ^* or $\sigma^* + L^*$) from a given N^*, we use extrapolation of the phenomenological dependence of N on σ ($N \propto \sigma^3$) to estimate σ^*. For dumbbells, we subsequently add L^* (which can be calculated from L/σ and σ^*) 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 $d/\sigma \approx 0.52$, (corresponding to a slightly protruded hemisphere). Note that for $d/\sigma > 0.5$, 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
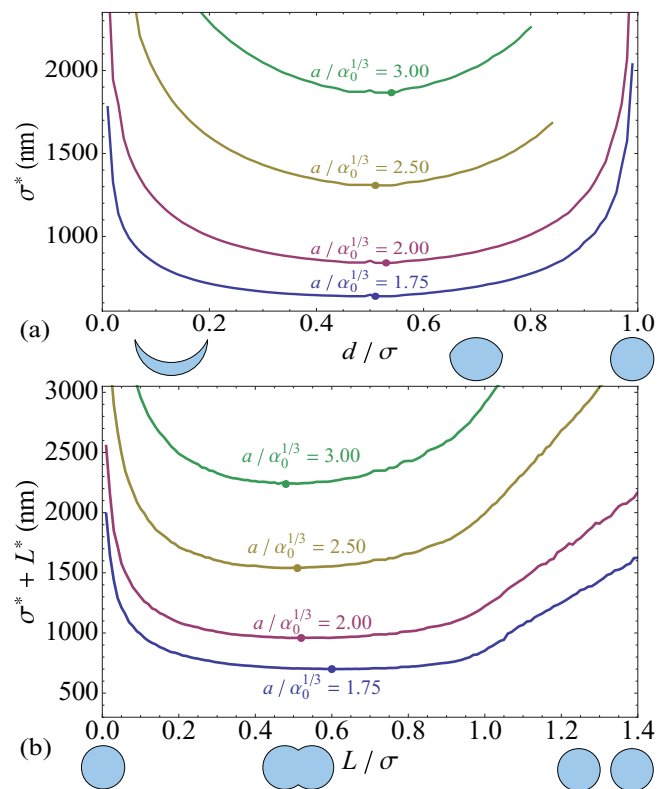
FIG. 4. The size parameter σ^* (a) and $\sigma^* + L^*$ (b) for which colloidal bowls and dumbbells, respectively, first become alignable by an electric field $E_0 = 100 \text{Vmm}^{-1}$, as a function of their shape parameters d/σ and L/σ, respectively. Here, d is the thickness of a bowl and L is the 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 $a/\alpha_0^{1/3} = 1.75, 2, 2.5,$ and 3. The temperature is $T = 293\text{K}$, and the atomic polarizability is $\alpha_0 = 5.25$ Å^3. The dots denote the minima in the graphs.

graphs are more strongly dependent on the shape when the coupling is weak (high $\tilde{a}$). With weak coupling, it is apparently more important that the particle has exactly the right shape.

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[40] Other choices for the definition of size parameter are possible, with the condition that it, together with the shape parameter, fixes the dimensions of the particle. For example, a possibility would be to define the size parameter as the diameter of the particle's circumscribed sphere. Qualitatively, this new definition does not cause any change to our results; quantitatively, we observe that the minima for rods shift to $l/L \approx 0.47$ and those for platelets to $L/l \approx 0.32$, while there is no change for bowls and dumbbells (since the size parameter remains σ and $\sigma + L$, respectively).
[41] The reason why a lower lattice constant lowers L^* or l^* is two-fold: a lower lattice constant means that atoms interact more and hence will have a higher Δ_f; at the same time it also means that the atom density is higher and thus smaller dimensions are needed to achieve a certain number of atoms.