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Coupled electrostatic and material surface stresses yield anomalous particle interactions and deformation

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Like-charges repel, and opposite charges attract. This fundamental tenet is a result of Coulomb’s law. However, the electrostatic interactions between dielectric particles remain topical due to observations of like-charged particle attraction and the self-assembly of colloidal systems. Here, we show, using both an approximate description and an exact solution of Maxwell’s equations, that nonlinear charged particle forces result even for linear material systems and can be responsible for anomalous electrostatic interactions such as like-charged particle attraction and oppositely charged particle repulsion. Furthermore, these electrostatic interactions and the deformation of such particles have fundamental implications for our understanding of macroscopic electrodynamics.

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I. INTRODUCTION

The controversy over electromagnetic momentum and stress in dielectrics has been one of the most debated topics in physics over the last century. The debate has centered around rival forms of the energy-momentum tensor in classical electrodynamics. While optical momentum receives significant attention, the debate has implications as to the distribution of electromagnetic stresses in materials. Because of this, conclusions drawn from the broader field of electrodynamics should shed light on the physics of electrostatic systems.3

The prevailing modern view is that the various formulations of electrodynamics represent different divisions of the total energy-momentum tensor. Mathematically, the total system can be separated into a number of subsystems (i.e., electromagnetic, material, etc.) such that the four-vector

\[
\begin{bmatrix}
\tilde{f}_j \\
\varphi_j
\end{bmatrix} = \nabla \cdot \mathbf{S}_j = \begin{bmatrix}
\tilde{f}_j \\
\mathbf{S}_j/c \\
-W_j
\end{bmatrix}
\]

represents the momentum and energy transfer between subsystems indexed by \( j \). Here, \( \nabla = [\nabla, \partial/\partial (ic t)] \) is the 4-dimensional divergence, \( \tilde{r}_j \) is a momentum flux or stress tensor, \( \mathbf{S}_j \) is a power flux, \( \mathbf{G}_j \) is a momentum density, and \( W_j \) is an energy density. Momentum and energy conservation is expressed as \( \nabla \cdot (\sum_j \mathbf{S}_j) = 0 \). These quantities relate energy and momentum transfers to and from materials via the power density \( \varphi_j \) and force density \( \tilde{f}_j \), which are regarded as interaction terms between the electromagnetic subsystem and other subsystems representing the materials. Historically, contributions from field and material stresses have remained ambiguous. The field-kinetic momentum density \( \mathbf{G}_k \), which is common to the Abraham, Einstein-Laub, and Chu formulations of electrodynamics, is responsible for the overall center-of-mass translations of a material, while the canonical momentum associated with the Minkowski formulation is responsible for translations with respect to the surrounding medium.4

Recently, the field-kinetic subsystem was uniquely identified as the Chu formulation using translational invariance of physical laws.5 While the form of the momentum density \( \mathbf{G} \) does not factor in to electrostatic force calculations, the identification of the field-kinetic stress tensor does have implications for the physics of electrostatic stress and force distributions in materials since \( \tilde{f}_j = -\nabla \cdot \mathbf{F}_j \) in static systems. In particular, it describes the physics of anomalous electrostatic interactions such as the nonlinear nature of charged particle forces responsible for oppositely charged particle repulsion and particle deformation, as we demonstrate in this correspondence. This basic physics is important to the understanding and modeling of colloidal systems under external field control.

Non-uniform distributions of binary charged particle mixtures can self-assemble into larger structures, and the self-limiting growth process is dictated, in part, by a balance between van der Waals attraction and forces of electrostatic repulsion and attraction due to the distribution of size and charge in the system.6 The nonlinear nature of like-charged particle forces has been well studied experimentally, owing to two decades of anomalous like-charge attraction observations in colloidal suspensions.7-16 Theoretical models have been advanced to explain the phenomenon of like-charge attraction.17-22 Electrostatic models involving a charge-free background medium include: an analytical solution by Bichoutskaia et al., revealing that either size or charge asymmetry can result in attractive electrostatic force between like-charged particles; an analytical solution by Stace et al.,19 which requires redistribution of surface charge density to explain like-charge attraction; numerical solutions by Xu,21 demonstrate that size and charge asymmetry produces like-charge attraction; and numerical simulations by Murovec and Brosseau22 determine the repulsion-to-attraction crossover for various configurations of metallic spheres.
where the two particles are on the photonic surfaces.25,26 Conversely, Datsyuk and Pavlyuk recently studied submerged particle deformation using the kinetic force on particles.24 However, both of these views of the force distributions in the volumes and on the surfaces of submerged particles and submerging fluid are incomplete. Understanding the physics of both forms of anomalous forces and associated surface stresses are important in the study of colloidal self assembly6 and controlled assembly of systems used in emerging applications such as configurable photonic surfaces.25,26

In this correspondence, we show, using both an approximate description and an exact solution of Maxwell’s equations, that nonlinear charged particle forces result even for linear material systems and can be responsible for anomalous electrostatic interactions such as like-charged particle attraction and oppositely charged particle repulsion. In particular, the total electromagnetic and induced material stresses in the surrounding fluid are responsible for the observable motion and equilibria of colloidal spheres. Although the physics of such surface pressures has recently been questioned,24 we show that indeed the Minkowski stress, which is the sum of electromagnetic and material stress, is responsible for the observable effects in particle-particle interactions and surface deformations. Such nonlinear interactions can produce a stable potential well for a dissimilar particle in the vicinity of a larger particle.

II. METHODS

All calculations have been performed on PC’s using Matlab,6 and the fields and Minkowski force calculations are verified using COMSOL Multiphysics.6 Both approximate dipole and full analytical solutions were used for the solution of dielectric spheres in dielectric fluids.

A. Dipole approximation

A simple model of charged particle interaction in a charge-free, dielectric medium can be developed by expanding the electrostatic force up to the dipole terms. The force on a uniformly charged dielectric particle is \( F \approx (q + \bar{p} \cdot \nabla)E \), where \( E \) is the total electric field at the particle location and \( \bar{p} \) is the dipole polarization. The force on the top particle is

\[
F_1 \approx \left( q_1 + p_1 \frac{\partial}{\partial z} \right) E(z),
\]

where the two particles are on the \( z \)-axis and expressions for the total electric field \( E(z) \) and polarization \( p_1 \) have to be determined. The relative polarization is the dipole moment of a sphere \( p_1 = 4\pi e_0 R^2 (\xi_1^2 \xi_2 E_2 + \xi_2^2 \xi_1 E_1) \) with respect to the background, where \( \xi_j = (e_j - e_0)/(e_j + 2e_0) \) is the Clausius-Mossotti factor relating the dielectric permittivities of the particles \( e_j \) and the background medium \( e_0 \). The electric field \( E(z) \) in Eq. (2) is expanded by considering the fields due to both the monopole and dipole of the bottom particle \( (j = 2) \)

\[
E(z) \approx \frac{q_2}{4\pi e_0 z^2} + 2\xi_2^2 \left( \frac{R_2}{z} \right)^3 E_2.
\]

Substituting Eq. (3) into Eq. (2) yields an approximate equation for the force on the top particle at a distance \( z = d \) from the bottom particle

\[
F_1 = \frac{q_1 q_2}{4\pi e_0 d^2} - \frac{R_1^3 R_2^3}{d^4} \frac{R_1 R_2}{d^3} \frac{E_1 E_2}{2} + 2q_1 q_2 \left( \frac{R_2}{d} \right)^3 E_2 - 2q_2 \left( \frac{R_1}{d} \right)^3 E_1.
\]

The first term represents the Coulombic force on the particle monopoles, the second term gives dipole interactions between the particles, and the third and fourth terms yield the interaction between the monopoles and dipoles. The excitation fields \( E_1 \approx q_1/(4\pi e_0 d^2) \) and \( E_2 \approx -q_1/(4\pi e_0 d^2) \) are approximated for both particles as the field at the center of particle 1 due to the other particle monopole.

B. Analytical expansion

An exact, analytical solution to the multiple particles problem is also applied.27–29 The solution accounts for an arbitrary number of multiple particles, each with unique non-uniform surface charge, dielectric permittivity, and radius, although we consider only uniform surface charges. The electric potential internal and external to particle \( j \) is expanded in the spherical basis

\[
\psi_{\text{int}}^{(n)} = \sum_{n=-m}^{m} A_{nm}^{(j)} r^n p_{n}^{(j)} \cos(\theta_j) e^{im\phi_j},
\]

\[
\psi_{\text{ext}}^{(n)} = \sum_{n=0}^{m} \sum_{n=-m}^{m} B_{nm}^{(j)} r^{(n+1)} + W_{nm}^{(j)} r^n p_{n}^{(j)} \cos(\theta_j) e^{im\phi_j}.
\]

The coefficients give the magnitudes of the spherical modes internal to particle \( j (A_{nm}^{(j)}) \), external to the \( j \)th particle due to particle \( j (B_{nm}^{(j)}) \), and external to the \( j \)th particle due to all other sources besides particle \( j (W_{nm}^{(j)}) \). Therefore, the mode coefficients \( W_{nm}^{(j)} = \sum_{k \neq j} H_{nm}^{(jk)} \) include the field contributions from all other particles. \( H_{nm}^{(jk)} \) is calculated using the re-expansion theorem

\[
H_{nm}^{(jk)} = (-1)^{n} \Gamma_{nmnp} r_{kj}^{-(n+m+1)} P_{nm-n}^{(m+1)}(\cos \theta_j) e^{i(m-n)\phi_j},
\]

where \( P_{n}^{(m)}(\cdot) \) represents the Legendre function of the first kind, \( r_{kj}, \theta_{kj}, \phi_{kj} \) represents the coordinates from the origin at particle \( j \) to the particle \( k \) and \( r_{kj}', \theta_{kj}', \phi_{kj}' \) gives the particle \( k \) with respect to the image at \( j \), and

\[
\Gamma_{nmnp} \equiv i^{n-m-[|n|-n]} \sqrt{(n+m+\mu)(n-m+\mu)(n+m)(n-m)\mu}.
\]
The electric field is calculated from the potentials by $E = -\nabla \psi$. A unique field solution is obtained by application of the boundary conditions at the surface of each particle by translating each spherical expansion to every other particle vicinity.\textsuperscript{27} Integration of the Minkowski force density or surface integration of the associated stress tensor\textsuperscript{30} yields the observable force on the particle, assuming that the polarization is defined with respect to the background medium $\mathbf{P} = (\epsilon_\rho - \epsilon_b)\mathbf{E}$. The Minkowski force on each particle reduces to a simple sum of mode coefficients.\textsuperscript{31} Convergence to three significant figures has been demonstrated using $N=10$ modes for collections of touching spheres.\textsuperscript{28}

III. RESULTS

Consider two dielectric, uniformly charged particles each with a total surface charge $q_j$ and radius $R_j$ as shown in Fig. 1, where $j = 1, 2$ indicates the top or bottom particle, respectively. By expanding the dipole approximation depicted in Figs. 1(b) and 1(c), the force on the top particle in terms of the given parameters is

$$F_1 = F_0 \left\{ 1 + 6 \xi_1 \xi_2 \left( \frac{R_2}{d} \right)^3 \left( \frac{R_1}{d} \right)^3 - 2 \frac{q_1}{q_2} \xi_2 \left( \frac{R_2}{d} \right)^3 \right. \right.$$  
$$\left. - 2 \frac{q_2}{q_1} \xi_1 \left( \frac{R_1}{d} \right)^3 \right\},$$  

where $F_0 = q_1 q_2 / (4\pi \varepsilon_0 d^2)$. This relation assumes application of the Minkowski formulation of electrodynamics since the Clausius-Mossotti factors $\xi_j$ are defined with respect to the background fluid.\textsuperscript{1} Implications of this assumption are discussed later in this correspondence. Presuming that all dielectric permittivities are positive, a medium with $\xi_j \geq \xi_b$ will result in a relative Clausius-Mossotti factor in the range $0 \leq \xi_j \leq 1$, while an inverted system ($\epsilon_j < \epsilon_b$) will result in $-0.5 < \xi_j < 0$.

Figure 1 illustrates the force given in Eq. (9). A uniformly charged spherical particle with total charge $q_1$ is subject to Coulombic attraction or repulsion to a second charge $q_2$ at some distance $d$. The monopoles $q_j$ induce dipole moments in the opposite particle. The monopole-monopole and dipole-dipole interactions act in the same direction as $F_0$. However, the monopole-dipole interactions can reverse the overall direction of the force. For example, when the system is inverted such that $\xi_1, \xi_2 < 0$, the dipoles depicted in Fig. 1(c) are reversed to produce repulsive monopole-dipole forces. Note that in this model the relative values of $\xi_j$ are used and such that all of the force is computed on the particles with zero force on the surrounding fluid.

Like-charged particles tend to form a repulsive pair since $F_0 > 0$, and oppositely charged particles tend to form an attractive pair since $F_0 < 0$. In order to obtain an anomalous force, the monopole-dipole terms in Eq. (9) should dominate. For like-charge attraction, $q_1/q_2 > 0$, and we consider $\xi_1, \xi_2 > 0$. Opposite-charge repulsion requires that the material system be inverted so that $\xi_1, \xi_2 < 0$, since $q_1/q_2 < 0$. The resulting approximate condition for either case of anomalous force is

$$1 + 6|\xi_1||\xi_2| \left( \frac{R_2}{d} \right)^3 \left( \frac{R_1}{d} \right)^3 - 2 \frac{|q_1|}{|q_2|} |\xi_2| \left( \frac{R_2}{d} \right)^3$$  
$$+ 2 \frac{|q_1|}{|q_2|} |\xi_1| \left( \frac{R_1}{d} \right)^3.$$ (10)

Two simple cases of interest are particles of the same size ($R_1 = R_2 = R$) and particles of significantly different size ($R_2 \gg R_1$), both consisting of the same material ($\xi_1 = \xi_2 = \xi$). First, Eq. (10) simplifies to $|q_1|/|q_2| > 4|\xi|^{-1} + \frac{1}{2} |\xi|$ for particles of the same size and $|q_1| \gg |q_2|$. Second, we find that $|q_1|/|q_2| > \frac{1}{2} |\xi|^{-1}$ when $R_2 \gg R_1$. Note that this second

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Two dielectric particles with uniform surface charge densities and positive polarization responses. (a) The equivalent fields and forces up to a dipole approximation are depicted by the superposition of interactions between the monopoles and dipoles for (b) like-charged particles and (c) oppositely charged particles. $q_j$ is the total charge and $\mathbf{p}_j$ is the polarization for the top ($j = 1$) and bottom ($j = 2$) particle.}
\end{figure}
case includes particles of about the same total charge since \( \zeta \) tends to be in the order of 1. Therefore, we can expect that like-charge attraction and opposite-charge repulsion may occur when a significant disproportion in size, charge, or both exists.

Example calculations for the force on the top particle \( F_1 \) are shown in Figs. 2 and 3. For comparison, the dipole approximations (markers) are plotted with the full analytical expansion (lines). The particles are like-charged with similar radii in Fig. 2(a), and unequal radii in Fig. 2(b). It is apparent from the plots that same size particles can experience like-charge attraction, and particles with significantly disproportionate sizes can exhibit like charge attraction even when the total particle charges are equal. Figure 3(a) indicates that opposite charge repulsion also occurs for similar sized particles when \( |q_1/q_2| \) is significantly greater than unity. Again, we see in Fig. 3(b) that opposite-charge attraction can occur with particles of equal total charge if a significant difference in size exists.

IV. DISCUSSION

Two important differences between like-charge attraction and opposite-charge repulsion justify further discussion.

First, oppositely charged particle interaction results in a non-contact equilibrium separation, while like-charged particle forces results in a unstable null force location. In other words, two oppositely charged particles can exhibit an energetically stable equilibrium at some nonzero separation distance that should be subject to experimental verification. Second, opposite-charge repulsion requires an inverted material system such that the background dielectric permittivity is greater than that of the particles. Materials will generally have static permittivities greater than one requiring the background fluid to have a relatively large dielectric permittivity.

While describing the dipole approximation of the particle forces, the particle relative polarization was specifically defined with respect to the background medium. This is equivalent to computing the force on the particle using the divergence of the Minkowski stress. In this description, the entire force is attributed to the two particles. However, the prevailing physical theory of electrodynamics describes an electrostatic force on both particles and the surrounding dielectric fluid, while the Minkowski formulation provides a simpler computational means.\(^1,2\)

As an illustration, consider a pair of particles where \( \epsilon_1 = \epsilon_2 = \epsilon_0 \) represents an air bubble. If particle 1 is uncharged...
and subject to the field due to charged dielectric particle 2, the true electrostatic force on particle 1 is zero. This is because its actual, not relative, polarization is zero. In an experiment, an apparent force on both particles will be observed due to the force and resulting stress in the surrounding fluid.

This is analogous to optical forces where air bubbles experience both a radiation pressure force and a gradient force in spite of their null polarization. Optical particle trapping occurs due to the balance of a scattering force due to radiation pressure and a trapping force due to the gradient of field intensity, the latter of which is exerted upon both the particle and the surrounding liquid.

In oppositely charged particle repulsion, the attractive Coulomb force between the free charges is countered by the gradient force on the particle and the surrounding liquid. Since the gradient force is also attractive in nature, an inverted material system can create a stable electrostatic equilibrium because the pulling force on the background liquid is stronger than that on the particle, creating a net difference of repulsion on the particle. The resulting potential energy $\Phi$ is derived from the total force $\mathbf{F} = \nabla \Phi$ and results in a potential well demonstrated in Fig. 4. The potential well results from a balance of attractive electrostatic forces on both the particle and the surrounding fluid given by the field-kinetic subsystem of electrodynamics, and the material stress

$$\mathbf{T}_{\text{total}} = \mathbf{T}_{\text{mech}} + \mathbf{T}_{\text{Min}} = \mathbf{T}_{\text{mech}} + \mathbf{T}_{\text{mat}} + \mathbf{T}_{F_s},$$

(11)

where the stress tensor $\mathbf{T}_{\text{mech}}$ represents an external mechanical input of work that would be required to keep the particles from accelerating, $\mathbf{T}_{\text{mat}}$ is associated with the material response subsystem, and $\mathbf{T}_{F_s}$ represents the field-kinetic subsystem stress tensor. In other words, $\mathbf{T}_{F_s} = \frac{1}{2}(\epsilon_0 \mathbf{E} \cdot \mathbf{E}) \mathbf{j} = \epsilon_0 \mathbf{EE}$ describes the electromagnetic stress in any material or vacuum region and $\mathbf{T}_{\text{mat}} = \frac{1}{2}(\mathbf{F} \cdot \mathbf{F}) \mathbf{j} - \mathbf{FF}$ gives any induced stress in the material. It is the sum of these two stresses that produces the surface pressures that are described by the Minkowski stress $\mathbf{T}_{\text{Min}} = \frac{1}{2}(\mathbf{D} \cdot \mathbf{E}) \mathbf{j} - \mathbf{DE}$ and is responsible for the observable effects in dielectric fluids.

This physical description has recently been questioned by Datsyuk and Pavlyuk, who claim that only the “Lorentz” force, which is equivalent to the Chu or field-kinetic force in electrostatic systems, can model deformation of neutral particles by an applied, uniform electric field. Their approach calculates the static surface pressures on spheres in a submerging background fluid with zero conductivity ($\sigma_b = 0$) and showed that the field-kinetic pressure best describes the experimental results published in Ref. 34. However, the model of a nonconducting submerging fluid approximates the high-frequency limit of an oscillating electric field. This is because the period of oscillation $T$ is much less than the time-constant of the medium $\tau_b = \epsilon_b/\sigma_b$ since free charges do not have time during the half-cycle of the electric field to redistribute non-uniformly on the surface of the sphere. The analytical field solution in this case ($T \ll \tau_b$) converges to the dielectric case

$$\psi_{\text{int}}^{\text{HF}} = -3E_0 \left( \frac{c_b}{\epsilon_b + 2\epsilon_b} \right) r \cos \theta,$$

(12a)

$$\psi_{\text{ext}}^{\text{HF}} = E_0 \left( \frac{\epsilon_p - c_b}{\epsilon_p + 2c_b} \right) \left( \frac{a}{r} \right)^3 r \cos \theta.$$

(12b)

The resulting surface pressure predicts deformation into an oblate spheroid for the field-kinetic (Lorentz) stress and a prolate spheroid for the Minkowski stress as shown in Fig. 5, which agrees with the calculations presented in Ref. 24.

However, in the low-frequency limit $T \gg \tau_b$, the charges relax during each half cycle to extinguish the tangential fields at the surface of the sphere. The resulting analytic field solution is

$$\psi_{\text{int}}^{\text{HF}} = -\frac{3}{2} E_0 r \cos \theta,$$

(13)

$$\psi_{\text{ext}}^{\text{HF}} = -\frac{1}{2} E_0 \left( \frac{a}{r} \right)^3 r \cos \theta.$$

(14)

The resulting surface pressure predicts deformation into an oblate spheroid for both the field-kinetic (Lorentz) and Minkowski stresses as shown in Fig. 6. This result agrees with the (group 16) results of Ref. 34, which experimentally demonstrated that such an inverted system ($\epsilon_p < \epsilon_b$) with conducting fluid background induces a prolate spheroid at 60 Hz and an oblate spheroid at 0 Hz uniform applied field. This frequency-based switching behavior is not predicted in Ref. 24.

V. CONCLUSIONS

In summary, we have shown that using both an approximate description and an exact solution of Maxwell’s equations, nonlinear charged particle forces result even for linear material systems and can be responsible for anomalous electrostatic interactions such as like-charged particle attraction...
and oppositely charged particle repulsion. Furthermore, oppositely charged particles in an inverted dielectric system can produce stable equilibrium potential wells at some separation distance. The physics of these interactions is described by the total stress on the particle and the background fluid. We have presented the results using unity dielectric constant spheres to illustrate the contrast between the force on the submerging fluid and that on the particle since the particle dipole force is zero for $\varepsilon_p = \varepsilon_0$. However, the results presented here are general and fundamentally dependent upon the contrast between the particle dielectric and the background with the field-kinetic (Chu or Lorentz) subsystem representing the correct separation of the coupled field/material (Minkowski) stress. Furthermore, we have illustrated that the observable forces and pressures resulting in particle deformation are described by the Minkowski stress, which results from the sum of field stress and induced material stress. Yet, multi-physics modeling of particle and fluid dynamics results from the electromagnetic (field-kinetic) subsystem separated from material subsystems. The observable optical pressure as a coupling of field and fluid stresses in submerging dielectrics has also been debated over the past few years.\textsuperscript{33,35–37} Thus, experimental measurement of the stable equilibrium separation of a pair of oppositely charged dielectric particles in an electrostatically dense background fluid would provide a fundamental test of electrodynamics, as well as provide insight into the modeling of colloidal self-assembly. Such observations could be made utilizing a microscope and CCD system previously applied to record like-charged attraction in microscopic particle systems,\textsuperscript{11,14} and these predictions also apply to sub-micrometer systems of colloidal nanoparticles.

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