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A theory of interactions between polarizable dielectric spheres

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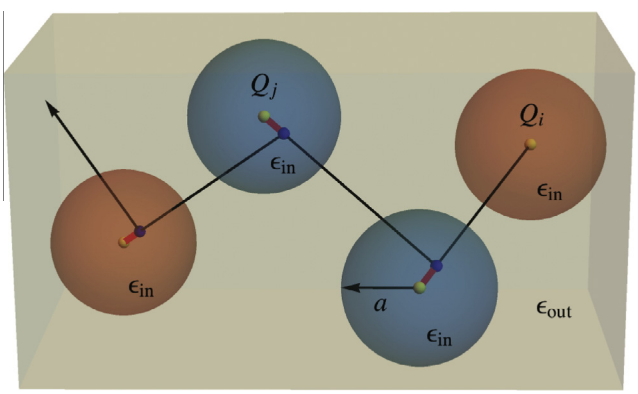
GRAPHICAL ABSTRACT



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ABSTRACT

Surface charging or polarization can strongly affect the nature of interactions between charged dielectric objects, particularly when sharp dielectric discontinuities are involved. By relying on a generalized image method, we derive an analytical, perturbative theory of the polarization and the interactions between charged particles in many-body systems. The validity and accuracy of the theory are established by comparing its predictions to full-blown numerical solutions. The importance of polarizability is then demonstrated for clusters of dielectric spheres, as well as a periodic crystal of charged dielectric spheres arranged into a NaCl-type lattice. The analytical framework for understanding the consequences of polarization will enable molecular simulations of large systems of polarizable particles.

1. Introduction

Electrostatic interactions are ubiquitous in nature and technology [1,2]. Free charges, such as ions, respond to applied electric fields by generating a net current, whereas uncharged materials become polarized and generate additional electric fields whose magnitude and effects on charged and uncharged objects are

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largely determined by the relative dielectric permittivity of the material and its surroundings.

The dielectric response to an applied field changes abruptly at an interface where surface charges accumulate when both sides of the interface respond differently. Charge accumulation can influence the interactions between dielectric objects in profound ways. Examples include the aggregation or dispersion of charged granular materials [3,4], colloids [2], and nano-particles [5]. It also plays a central role in the clustering of dust involved in the early stages of planet formation [6–8].

Important efforts have sought to capture polarization effects in numerical calculations [9–13]. Some of the latest and more numerically-efficient approaches use explicit surface-charge elements to highlight the importance of polarization in charged colloidal particle assemblies [14,15]. Numerical methods, however, become unwieldy for studying polarization and its many consequences in large many-body system. This work presents a tractable and general analytical theory of many-body polarizability based on the extension of a multiple scattering formalism that obviates the need for surface charges and, instead, describes their overall influence of electrostatic interactions through analytical functions of only particle positions. As such, the theory is particularly well suited for description of many-body systems.

2. Theory

We consider an ensemble of dielectric spheres immersed in a continuum dielectric medium with dielectric permittivity ϵ_{out}, as illustrated in Fig. 1. A sphere i centered at $\mathbf{R}_i$ has dielectric constant $\epsilon_{\text{in},i}$, radius a_i, and charge Q_i. The theoretical underpinnings of our proposed approach are discussed in Refs. [16,17]. For simplicity, the spheres have uniform radii and dielectric constants, but different charges at the centers. However, the new formalism applies for different sizes and dielectric permittivities. The electrostatic energy for an arbitrary particle configuration is given by a multiple scattering series with terms of increasing complexity that depend on the relative positions of an increasing number of particles [16,17],

$$E = E_1 + E_2 + E_3 + E_4 + \cdots \qquad (1)$$

where $E_1 \equiv \sum_i \frac{Q_i^2}{8\pi a_i}\left(\frac{1}{\epsilon_{\text{out}}} - \frac{1}{\epsilon_{\text{in}}}\right)$ includes effectively contributions from Bohr solvation energies, which represent the interactions between the induced surface charges and the source charges at the centers of the spheres. The second term in the series, E_2, designates the effective two-body contributions, which equal the bare

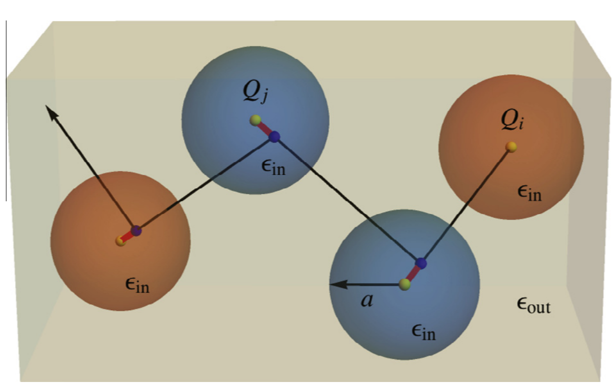

Fig. 1. The continuum model for an ensemble of dielectric spheres. Blue dot: Kelvin image point. Red segment: Neumann image line representing polarization effects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Coulomb energy between charges, $E_2 = \frac{1}{2}\sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_{\text{out}}|\mathbf{R}_i - \mathbf{R}_j|}$. The term $E_3 = \sum_{i,k,j} \frac{Q_i Q_j}{8\pi\epsilon_{\text{out}}} I_{ikj}$ includes the lowest-order polarization contributions to the energy, where the geometrical kernel I_{ikj} is given by

$$I_{ikj} = \left(1 - \frac{\epsilon_{\text{in}}}{\epsilon_{\text{out}}}\right) \int \frac{d\mathbf{S}_k}{4\pi \mid \mathbf{R}_i - \mathbf{r}_k \mid} \cdot \nabla_k \frac{1}{\mid \mathbf{r}_k - \mathbf{R}_j \mid}. \qquad (2)$$

Here $d\mathbf{S}_k$ is the surface element of the kth particle, $\mathbf{r}_k$ is the position vector, and ∇_k is the gradient with respect to $\mathbf{r}_k$. The terms in E_3 include the interaction between the surface charges induced by each source charge on all other charges in the system, thereby representing the effective interaction between two charges as mediated by the polarization arising at spherical interfaces. In principle, the source charge and the field charge can reside on the same sphere, but the scattering surface must be associated with a distinct particle.

Similarly, E_4 represents the second-order polarization contributions due to the interaction between two charges mediated by two polarized surfaces. Higher order terms follow in a similar manner, and all include geometrical kernels of the form $I_{ik_1k_2j}, I_{ik_1k_2k_3j}$, etc., as defined in Supplementary Materials (Eq. (7)). The theory has the important feature that these kernels are analytic function of the particle positions, thereby enabling straightforward calculation of the forces acting on all particles and facilitating a physical interpretation of individual terms in the expansion of Eq. (1).

A key extension of the theory, introduced in this work, is the summation of an infinite series of contributions in Eq. (1), resulting the conversion of two-dimensional integrals over surface charges into an equivalent form that involves considerably more tractable one-dimensional integrals over line charge densities. Ref. [17] and Supplementary materials show how the integral kernels $I_{ikj}, I_{ikkj}, I_{ikkkj}\cdots$ with identical first (i) and last (j) indices and with repeated internal (k) indices can be re-summed altogether, yielding

$$I_{ikj} + I_{ikkj} + I_{ikkkj} + \cdots = \epsilon \frac{t}{\sqrt{R_{ik}R_{jk}}}\left(\delta_{f,t^2} - gt^{-2g}\int_0^{t^2} \mathrm{d}f f^{g-1}\right)\frac{1}{\mathcal{D}_{ikj}}, \qquad (3)$$

where $\epsilon \equiv (\epsilon_{\text{in}} - \epsilon_{\text{out}})/(\epsilon_{\text{in}} + \epsilon_{\text{out}})$, $g \equiv 1/(1 + \epsilon_{\text{in}}/\epsilon_{\text{out}})$, $t \equiv a_k/\sqrt{R_{ik}R_{jk}}$, $\mathcal{D}_{ikj} = \left(1 + f^2 - 2f\hat{\mathbf{R}}_{ik}\cdot\hat{\mathbf{R}}_{jk}\right)^{1/2}$, and $\hat{\mathbf{R}}_{ik}$ and $\hat{\mathbf{R}}_{jk}$ are unit vectors pointing along the directions of $\mathbf{R}_{ik}$ and $\mathbf{R}_{jk}$ respectively. The term δ_{f,t^2} in parentheses represents the contribution from an image charge placed at the Kelvin point [18], which is conventionally used to represent the electrostatic field generated by the surface charge on a conducting sphere (see Fig. 1). The generalization here to describe the field produced by the dielectric spheres consists of a contribution from the image at the Kelvin point and augmented by an image line segment between the center of the sphere ad the Kelvin point (see Fig. 1). The contribution from the line segment was first documented by Neumann [19] over 130 years ago, and has been rediscovered several times [20–22] in different contexts, including the description of hydrodynamic interactions between small spherical particles in the neighborhood of large spherical particles [23]. Our work derives the analytic generalization of this image line charge construct to describe the many-body electrostatic interaction energy for a system with an arbitrary number of spherical particles – a generalization that is required for the evaluation of E_4, E_5, and all higher order contributions. In the Supplementary Materials, iterative yet explicit expressions are provided for the kernels needed to evaluate these higher order many-body interactions.

The magnitude of subsequent terms in Eq. (1) decreases as the number of intervening scattering surfaces increases. The convergence rate is governed by the mismatch in the dielectric