A theory of interactions between polarizable dielectric spheres

Jian Qin^{a,b,c,*}, Jiyuan Li^a, Victor Lee^{d,e}, Heinrich Jaeger^{d,e}, Juan J. de Pablo^{a,b,*}, Karl F. Freed^{f,e,*}

^a*Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, USA*

^b*Argonne National Laboratory, Lemont, Illinois 60439, USA*

^c*Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA*

^d*Department of Physics, University of Chicago, Chicago, Illinois 60637, USA*

^e*James Franck Institute, University of Chicago, Chicago, Illinois 60637, USA*

^f*Department of Chemistry, University of Chicago, Chicago, Illinois 60637, USA*

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.

Keywords: polarization, dielectrics, image method, particulate aggregate

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

*Corresponding author

Email addresses: jianq@stanford.edu (Jian Qin), depablo@uchicago.edu (Juan J. de Pablo), freed@uchicago.edu (Karl F. Freed)

Figure 1: The continuum model for an ensemble of dielectric spheres. Blue dot: Kelvin image point. Red segment: Neumann image line representing polarization effects.

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, 7, 8].

Important efforts have sought to capture polarization effects in numerical calculations [9, 10, 11, 12, 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 $\epsilon_{in,i}$, 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],

$$E = E_1 + E_2 + E_3 + E_4 + \dots \quad (1)$$

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 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

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

Here $d\mathbf{S}_k$ is the surface element of the k th 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 $I_{ik_1 k_2 j}$, $I_{ik_1 k_2 k_3 j}$, 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} , $I_{ikkkj} \dots$ with identical first (i) and last (j) indices and with repeated internal (k) indices can be re-summed altogether, yielding

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

where $\epsilon \equiv (\epsilon_{\text{in}} - \epsilon_{\text{out}})/(\epsilon_{\text{in}} + \epsilon_{\text{out}})$, $g \equiv 1/(1 + \epsilon_{\text{in}}/\epsilon_{\text{out}})$, $t \equiv a_k/\sqrt{R_{ik} R_{jk}}$, $\mathcal{D}_{ikj} = (1 + f^2 - 2f \hat{\mathbf{R}}_{ik} \cdot \hat{\mathbf{R}}_{jk})^{1/2}$, 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

Figure 2: (a) Electrostatic energy between two dielectric spheres. Points: numerical solution [15]; lines: Coulomb (blue) and polarization (1st and 3rd order nearly overlap) contributions. Ratios of charges and permittivities: $Q_1/Q_2 = 15$ and $\epsilon_{\text{in}}/\epsilon_{\text{out}}$ is 10. (b) Regimes of interactions: purely repulsive versus attractive at small separation. The first and third order theories nearly overlap.

image at the Kelvin point and augmented by an image line segment between the center of the sphere and 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, 21, 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 permittivity $\epsilon_{\text{in}}/\epsilon_{\text{out}}$, which determines the amount of surface charge, and the ratio between the sphere radius and the average inter-sphere separation, which measures the strength of electric field. The contributions $\tilde{E}_n$ ($n > 2$) to the total energy

$$E = E_1 + E_2 + \tilde{E}_3(g)\epsilon + \tilde{E}_4(g)\epsilon^2 + \dots \quad (4)$$

scale in the limit of large inter-particle separations as

$$\tilde{E}_n \simeq \frac{l_B}{d} \left(\frac{a}{d} \right)^{3(n-2)} k_B T, \quad (5)$$

where $l_B \equiv e^2/(4\pi\epsilon_{\text{out}}k_B T)$ is the Bjerrum length, a is the radius of the particles, and d is the average separation between particles. The exponent 3 arises because the dominant component of the polarization at large separations is given by the dipole moment, which is proportional to the volume of the particles. Note that here we use the standard definition for the Bjerrum length to illustrate the scaling dependence of energy on the different parameters. The actual system energy should scale quadratically with the charge per particle.

The polarization effects can be understood by considering a point charge Q_1 placed at $\mathbf{R}_1$, in the neighborhood of a dielectric sphere at the origin. The total electrostatic potential includes the Coulomb contribution and the contribution coming from the induced surface charge, which equals the sum of contributions from the Kelvin point and the Neumann line. The full expression for the electrostatic potential at position $\mathbf{R}_2$ is derived from Eq. (3). If the separations R_1 and R_2 are large, the dominant term is given by $Q_1 \frac{\epsilon}{1+g} \frac{t^3}{\sqrt{R_1 R_2}} \hat{\mathbf{R}}_2 \cdot \hat{\mathbf{R}}_1$, with $t \equiv a/\sqrt{R_1 R_2}$ [17]. This is precisely the electrostatic field generated by a surface charge dipole $\frac{\epsilon}{1+g} Q_1 t^3$. Higher order multipole terms may be constructed similarly, but the multipole expansion converges slowly at very short separations.

The field generated from a single scattering surface is greatly simplified in three limits: (1) when the dielectric permittivity approaches infinity, $\epsilon_{\text{in}} \rightarrow \infty$, the result reduces to that for a conducting sphere; (2) when the radius a asymptotically approaches infinity, the result reduces to that for a flat surface; and (3) when the electrostatic field acts on the source charge, the self-energy emerges in closed form, $Q_1^2 \epsilon \frac{t}{R} \left(\frac{1}{1-t^2} - \frac{g}{t^2 g} \mathbf{B}(t^2; g, 0) \right)$, where $\mathbf{B}$ is the incomplete Beta function.

3. Results

We next illustrate examples showing the importance of polarization effects. First, consider the interaction between two identical dielectric spheres with charges Q_1 and Q_2 . The Born solvation energy E_1 only shifts the energy by a constant and is inconsequential to the present discussion. The bare Coulomb energy $E_2 = Q_1 Q_2 / R_{12}$ for two like charges is purely repulsive, while the dominant polarization contribution E_3 becomes attractive if the particle's dielectric constant ϵ_{in} exceeds the medium value ϵ_{out} . This term can formally be written as

$$E_3 = (Q_1^2 + Q_2^2) \frac{f(a/R_{12}; \epsilon)}{R_{12}}. \quad (6)$$

The factor Q_1^2 (Q_2^2) originates from the interaction between the charge Q_1 (Q_2) and its image charges on particle 2 (1). The function $f(a/R)$ is given by Eq. (3), which depends on the details of surface charges, is negative (attractive), and is generally much smaller than unity.

Figure 3: (a) Electrostatic energy between three spheres in a triangular arrangement ($Q_1 = -0.25$, $Q_2 = Q_3 = 1$, $\epsilon_{\text{in}}/\epsilon_{\text{out}} = 10$). Lines: predictions of multiple scattering theory; points: numerical solution. (b) Stability diagram for close contact triangular configuration with $Q_2 = -Q_1$.

The ratio between E_3 and E_2 may be written as $E_3/E_2 = (Q_1/Q_2 + Q_2/Q_1) f(a/R_{12}; \epsilon)$. The interaction between the particles is therefore dominated asymptotically by the repulsive Coulomb contribution. However, E_3 may become more substantial than E_2 for sufficiently large charge asymmetry at short separations between the particles. This is confirmed by calculations presented in Fig. 2, for $Q_1/Q_2 = 15$ and $\epsilon_{\text{in}}/\epsilon_{\text{out}} = 10$, where at small separations the energy becomes purely attractive, owing to the surface charge polarization. Our results agree quantitatively with those obtained by full-blown numerical solution of the surface charges, where indeed the lowest order polarization contribution E_3 captures much of the polarization effect, and appears to be nearly 100 times faster than the numerical calculations.

A “phase” diagram designating the nature of two particle interactions is generated by varying the ratios $\epsilon_{\text{in}}/\epsilon_{\text{out}}$ and Q_1/Q_2 . Fig. 2 demonstrates the existence of a widening window of attraction as $\epsilon_{\text{in}}/\epsilon_{\text{out}}$ or Q_1/Q_2 increases, since a growth in either of them favors a stronger polarization interaction. Fig. 2(a) suggests that different orders of polarization contributions exhibit an oscillatory convergent behavior, and that E_3 alone is sufficient for small $\epsilon_{\text{in}}/\epsilon_{\text{out}}$, for which a closed-form expression is provided in the supplementary materials.

We next consider aggregates of three particles, with charges Q_1 , $Q_2 = -Q_1$ and Q_3 , arranged in a close-packed triangular configuration. The convergence rate of our theory is demonstrated in Fig. 3(a), and a stability diagram is presented in Fig. 3(b). The close-packed triangular configuration is unstable for all values of Q_3 in the absence of polarization effects, a consequence of the frustra-

tion experienced by particle 3 which repels particle 1 (2) for positive (negative) Q_3 . However, this frustration can be alleviated by sufficiently large polarization effects. Energy landscape and gradient calculations indeed show that increasing dielectric permittivity opens a stability window for finite Q_3 , and the region of stability is symmetric with respect to inverting the sign of Q_3 .

For larger clusters with N particles, the number of n -body terms is given by combinatorial factors of order N^n , which raises concerns on convergence. Our calculations, however, indicate that the condition of charge neutral system at large separations improves the convergence rate for higher order terms. So the growth of the combinatorial factor poses no problems. This feature is demonstrated for the worst possible case, i.e., that of $N \rightarrow \infty$ particles. Thus, we calculate the cohesive energy for a crystal of charged, polarizable particles arranged into a NaCl lattice. The “cationic” and “anionic” particles have equal size and form close contacts. Furthermore, in practice, since most of the contributions retained formally involve terms that vanish essentially when the separation between spheres is high, a distance cutoff can be introduced to reduce the number of terms to be evaluated.

The cohesive energy for ordinary crystals is the average Coulomb energy per site, the Madelung constant that equals -0.437 [24]. The many-body polarization corrections begin with E_3 , followed by E_4 , etc. This particularly system is interesting because the convergence rate with respect to order is low due to the large number of combinatorial factors and the long range nature of the Coulomb energy. We therefore examine these issues by studying the dependence of cohesive energy on system size and by extrapolating to an infinite lattice. The largest system considered contains 9^3 particles (Using an odd number of particles allows us to identify a particle at the center of the crystal and, to calculate the cohesive energy, we only need to evaluate the n -body terms to which this central point participates). Fig. 4 demonstrates that the first order contribution E_3 is negative for $\epsilon_{\text{in}}/\epsilon_{\text{out}} > 1$ and positive for $\epsilon_{\text{in}}/\epsilon_{\text{out}} < 1$. The second order contribution E_4 instead exhibits a maximum at $\epsilon_{\text{in}}/\epsilon_{\text{out}} = 1$ and is always negative. As expected, for the wide range of ϵ values investigated, E_3 is much smaller than E_2 , and E_4 is even smaller, presumably due to massive cancellations from the crystal’s symmetry at large distances. Our results represent the only available estimate of polarization effects in a nano-crystal, and additional, computationally-intensive convergence studies should be pursued in the future. We postulate that the relative stability of different types of lattices might be altered by the contributions of E_3 and E_4 , particularly in the presence of defects.

4. Summary

In summary, we have developed an analytic perturbative approach for evaluating the polarization energy for a many-body collection of charged dielectric spheres embedded in a dielectric medium. The polarization-induced interactions between these spheres depend on the ratio of dielectric constants for the spheres and the medium, and the ratio of the distance between particles and the radii of the particles. In some cases, polarization completely alters the

Figure 4: Electrostatic cohesive energy of a NaCl type lattice composed of charged, polarizable colloids, nano-particles, etc. The cations and anions have opposite charges and same radii, and form close contacts. Curves: first and second order polarization contributions.

qualitative behavior; e.g., the interaction energy for a two-particle cluster can switch from repulsive to attractive, depending on the charge asymmetry and dielectric contrast. In other cases, polarization leads to stable configurations that otherwise could not occur in its absence, e.g., three-particle close-packed arrangements. The polarization energy of the largest system considered here, namely a densely packed ionic-crystal in the form of an NaCl lattice, allows us to predict a generalized, permittivity-dependent Madelung constant that goes beyond existing predictions based solely on Coulombic interactions. These calculations imply that the polarization energy can become quite significant for aggregates of highly polarizable objects, and is thus relevant for study of the stability and kinetics of charged granular materials, colloids, and nanoparticles.

All the examples described here consider cases where the charges are placed at the center of particles, but the methodology can be readily applied to particles with arbitrary charge distributions to enable, in principle, investigations of the effects of polarization on the rotation of clusters of particles. The generalized image expansion introduced here could be further extended to describe the interactions among infinite dielectric cylinders, for which only the normal Kelvin images are needed. Furthermore, the methodology could also be applied to study the influence of electrostatic polarization on ion aggregation near a flat interface by representing the polarizable ion by a dielectric sphere,[17] and to study the polarization (image) effects on the ionic clouds surrounding a pair of highly charged interacting colloidal particles. Practical applications of our theory to clusters of specific systems, of course, will require inclusion of all other types of interactions. For example, the presence of van der Waals interactions yields contributions whose magnitude in the lowest order depends on the ratio of the Hamaker constant A [1] to the product of charges. The relative importance of the polarization term follows from its ratio with the leading order Coulomb interaction. As our theory demonstrates, polarization effects generally involve many-body particle interactions whose magnitude we can now evaluate analytically. Such effects may help interpret the nature of non-pairwise additive interactions that have been discussed in the literature on colloidal materials [2]. Importantly, the energy expressions developed here only depend on the par-

ticle positions and are thus ideally suited for molecular dynamics simulations and theoretical work. A subsequent paper will compare our calculations with experimentally determined trajectories of charged dielectric objects.

We acknowledge the support by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering at Argonne National Laboratory under Contract No. DE-AC02-06CH11357 (JQ and JdP), and under Award DOE-SC0008631 (KFF), and acknowledge the support by NSF DMR-1309611 (VL and HJ). The research project was formulated by KFF, JdP and HJ, the theory was formulated by JQ and KFF, the calculations were performed by JQ, JL, VL and KFF, and the manuscript was prepared by JQ, KFF and JdP. We are grateful to Erik Luijten for helpful discussions.

- [1] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York, 1992.
- [2] J. W. Merrill, S. K. Sainis, E. R. Dufresne, Many-body electrostatic forces between colloidal particles at vanishing ionic strength, *Phys. Rev. Lett.* 103 (2009) 138301.
- [3] S. R. Waitukaitis, V. Lee, J. M. Pierson, S. L. Forman, H. M. Jaeger, Size-dependent same-material tribocharging in insulating grains, *Phys. Rev. Lett.* 112 (2014) 218001.
- [4] V. Lee, S. R. Waitukaitis, M. Z. Miskin, H. M. Jaeger, Direct observation of kepler orbits and particle aggregation in charged granular streams, *Nature Physics* In press.
- [5] D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. Ye, J. Chen, C. B. Murray, Quasicrystalline order in self-assembled binary nanoparticle superlattices, *Nature* 461 (2009) 964–967.
- [6] J. Blum, G. Wurm, The growth mechanisms of macroscopic bodies in protoplanetary disks, *Annual Review of Astronomy and Astrophysics* 46 (2008) 21–56.
- [7] A. Zsom, C. W. Ormel, C. Guettler, J. Blum, C. P. Dullemond, The outcome of protoplanetary dust growth: pebbles, boulders, or planetesimals? II. introducing the bouncing barrier, *Astronomy & Astrophysics* 513 (2010) A57.
- [8] A. Kataoka, H. Tanaka, S. Okuzumi, K. Wada, Fluffy dust forms icy planetesimals by static compression, *Astronomy & Astrophysics* 557 (2013) L4.
- [9] R. Allen, J.-P. Hansen, Density functional approach to the effective interaction between charges within dielectric cavities, *J. Phys.: Condens. Mater* 14 (2002) 11981–11997.
- [10] R. Allen, J.-P. Hansen, S. Melchionna, Electrostatic potential inside ionic solutions conned by dielectrics : a variational approach, *Phys. Chem. Chem. Phys.* 3 (2001) 4177–4186.

- [11] J. P. Bardhan, R. S. Eisenberg, D. Gillespie, Discretization of the induced-charge boundary integral equation, *Phys. Rev. E* 80 (2009) 011906.
- [12] E. Cancès, B. Mennucci, J. Tomasi, A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics, *J. Chem. Phys.* 107 (1997) 3032.
- [13] S. Miertuš, E. Scrocco, J. Tomasi, Electrostatic interaction of a solute with a continuum. a direct utilization of ab initio molecular potentials for the prevision of solvent effects, *Chemical Physics* 55 (1981) 117–129.
- [14] K. Barros, E. Luijten, Dielectric effects in the self-assembly of binary colloidal aggregates, *Phys. Rev. Lett.* 113 (2014) 017801.
- [15] K. Barros, D. Sinkovits, E. Luijten, Efficient and accurate simulation of dynamic dielectric objects, *J. Chem. Phys.* 140 (2014) 064903.
- [16] K. F. Freed, Perturbative many-body expansion for electrostatic energy and field for systems of polarizable charged spherical ions in a dielectric medium, *J. Chem. Phys.* 141 (2014) 034115.
- [17] J. Qin, J. J. de Pablo, K. F. Freed, Image method for induced surface charge of dielectric spheres(to be submitted).
- [18] J. D. Jackson, *Classical Electrodynamics*, 3rd Ed., Wiley, 1998.
- [19] C. Neumann, *Hydrodynamische Untersuchungen nebst einem Anhang über die Probleme der Elektrostatik und der magnetischen Induktion*, Teubner, Leipzig, 1883.
- [20] I. V. Lindell, Electrostatic image theory for the dielectric sphere, *Radio Sci.* 27 (1992) 1–8.
- [21] R. Messina, Image charges in spherical geometry: Application to colloidal systems, *Journal of Chemical Physics* 117 (2002) 11062.
- [22] W. Cai, S. Deng, D. Jacobs, Extending the multipole method to charges inside or outside a dielectric sphere, *J. Comp. Phys.* 223 (2007) 846–864.
- [23] S. Kim, A new approach to hydrodynamic interactions in polydisperse suspensions, *Particulate Science and Technology* 6 (1988) 69–80.
- [24] C. Kittel, *Introduction to Solid State Physics*, Wiley, 1995.