Exact polarization energy for clusters of contacting dielectrics

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Abstract

The induced surface charges appear to diverge when dielectric particles form close contacts. Resolving this singularity numerically is prohibitively expensive because high spatial resolution is needed. We show that the strength of this singularity is logarithmic in both inter-particle separation and dielectric permittivity. A regularization scheme is proposed to isolate this singularity, and to calculate the exact cohesive energy for clusters of contacting dielectric particles. The results indicate that polarization energy stabilizes clusters of open configurations when permittivity is high, in agreement with the behavior of conducting particles, but stabilizes the compact configurations when permittivity is low.

For particle aggregates or clusters stabilized by electrostatic interactions,\textsuperscript{1–3} the cohesive energy depends on the dielectric permittivities of both the particles and the medium. Permittivity quantifies the density of dipoles induced by externally applied electric fields, which is proportional to polarization in the linear regime. When the permittivity contrast between the particles and the medium is high, as is often the case, the polarizations from the two sides of the interface do not fully compensate each other, resulting in the accumulation of induced surface charges.

Resolving the surface charges is needed to evaluating the electrostatic interactions among particles in close proximity, and is challenging because polarization is intrinsically a many-body effect, depending on the positions of all particles. For instance, careful measurements in colloidal suspensions have shown that the inter-particle force is non-additive, which is at least partially due to the polarization effect.\textsuperscript{4} In another set of experiments on metallic nanoparticles, it has been found that the aggregation of multiple particles surrounding a charged particle can be stabilized by the polarization effect alone.\textsuperscript{5} More dramatic demonstration of such polarization effects is found in the so-called like-charge attraction caused by the strong polarization effect, for particles of large size or permittivity ratios.\textsuperscript{6,7}

Computational methods, such as the boundary element method,\textsuperscript{8} the spectral methods,\textsuperscript{9,10} and the image method,\textsuperscript{11} have been developed to account for this polarization effect. In practice, these methods all need to evaluate the induced surface charge densities in one form or another, and have been successfully applied to study a wide range of problems involving the aggregation of polarizable particles.\textsuperscript{12–14} However, when particles are in close proximity, the surface charge densities apparently diverge because the electric field in the narrow gap region is strong even for a small difference in the electrostatic potentials of particles. This is analogous to the divergent lubrication force between approaching solid particles in the Stokesian regime.\textsuperscript{15} Resolving these apparently diverging charge densities requires a high spatial resolution that becomes computationally prohibitive for nearly touching particles.\textsuperscript{8} For conductors like metallic particles, the functional form of the divergent charge density has been identified and used to isolate the singularity obscuring numerical calculations, and to obtain the exact energy and force for contacting particles.\textsuperscript{5} For dielectric particles, the question remains unsolved.

![Figure 1: Surface charges between two particles separated by a distance $h$. The separation of two surfaces at a radial distance $r$ from the contact points can be approximated by $h + r^2/a$, where $a \equiv 2/(a_1^{-1} + a_2^{-1})$. The permittivity of the medium is $\varepsilon_{\text{out}}$. Surface of conducting particles are equipotential with potential set to $V$ and $0$. Surfaces of dielectric particles, with permittivities $\varepsilon_1$ and $\varepsilon_2$, have surface potential distributions $\phi_1(r)$ and $\phi_2(r)$, respectively.](image)
One way to reveal these singular surface charges is to consider two conducting particles separated by a small gap, as sketched in Fig. 1. The points on the two surfaces separated by the minimum distance, or gap distance \( h \), are referred to as contact points. The surface charge density is proportional to the strength of the normal component of electric field on surfaces, according to Gauss’s law. When \( h \) is small, the electric field lines in the gap region are nearly parallel to the line connecting the two contact points. The strength of the electrical field is, in turn, proportional to the difference in the surface electrical potentials. This relation between the surface potential and the electrical field is analogous to that between the longitudinal velocities of converging particles and the transverse velocity of squeezed fluid velocity in the lubrication theory.\(^{15}\)

To calculate the surface charge density, both the surface potentials and the vertical separations are needed. Since conductors are equipotential, the surface potentials can be set to \( V \) and \( 0 \) respectively. The vertical separation depends on the radial distance \( r \), and can be expressed within the Derjaguin approximation as \( h + r^2/a \), where \( a \) is the harmonic average of radii of curvature \( a_1 \) and \( a_2 \) at the two contact points, i.e., \( a^{-1} = (a_1^{-1} + a_2^{-1})/2 \). Here, the spherical apexes are assumed for simplicity, but more general curvatures can be treated similarly. Consequently, the field strength at radius \( r \) is \( E(r) = V/(h + r^2/a) \), and the surface charge density \( \sigma(r) = \frac{2\pi e}{\epsilon_0 V} V/(h + r^2/a) \) on the top surface, where \( \epsilon_0 \) is the medium permittivity. Integrating \( \sigma(r) \) for \( r \) from 0 to \( R_0 \), where \( R_0 \) is a cutoff of order \( a \), results in the singular part of the surface charge

\[
Q_s = \frac{V \epsilon_0}{4\pi} \int_0^{R_0} dr \frac{2\pi r}{h + r^2/a} \approx \frac{V \epsilon_0 a}{4} \ln \left( \frac{a}{h} \right).
\] (1)

The unity in the logarithmic term is dropped because \( R_0 \approx a \gg h \). Further, the difference between \( R_0 \) and \( a \) is neglected because it only leads to a constant shift. Equation (1) shows how surface charges of the upper surface become singular as the gap distance decreases. That of the lower surface is also singular, but of opposite sign. In the limit \( h \to 0 \), the energy does not blow up because the potential difference \( V \) vanishes once particles form contact.

The ratio of the singular charge \( Q_s \) and the potential difference \( V \) gives the singular part of the capacitance \( \epsilon_s = \epsilon_0 a \ln(a/h)/4 \), which has been found previous for spherical dimers.\(^{8,7}\) The above analysis shows that this singular capacitance is local. Thus, the same singularity applies to non-spherical particles, and for aggregates of multiple particles. This fact has been employed to find the exact energy for clusters of contacting, conducting particles.\(^{8,7}\) In this work, the full capacitance array is first numerically calculated for an ensemble of conducting particles at finite but small separations. The singular contribution is then subtracted, leaving a regular part that can be extrapolated to \( h = 0 \). Finally, when the singular and regular parts are pieced together, the variation of energy with separation is obtained.

For the dielectric case, a straightforward generalization of the above treatment fails, because the particles are not equipotential. The potential difference \( \Delta V(r) \) needed to evaluate the charge density in eq. (1) cannot be fully specified by the potential difference between the contact points \( \Delta V(0) \). The variation of \( \Delta V(r) \) with \( r \) in the gap region is expected to be quadratic, but the curvature is unknown a priori. In an early, and analogous work on thermal conduction of composite materials, Batchelor et al.\(^{12}\) noticed that the potential distribution, which determines the surface charges, is itself dominated by the contribution from the surface charges nearby, so that a self-consistent treatment is needed.

To illustrate this point, consider the dielectric case in Fig. 1. Let the surface potentials of the two particles be \( \phi_1(r) \) and \( \phi_2(r) \), and the surface charges be \( \sigma_1(r) \) and \( \sigma_2(r) \). The surface potential \( \phi_i(r) \), with \( i = 1, 2 \), can be calculated by integrating the coulombic potential of the respective surface charges. Near the contact point, we have

\[
\phi_i(r) = \hat{V}_i + \frac{1}{2\pi \epsilon_i} \int_0^{2\pi} d\theta' \int_0^{\pi} r' \sigma_i(r') \frac{d\theta'}{r'^2 + r'^2 - 2r'\cos\theta'}. \] (2)

Here, \( \hat{V}_i \) are the contributions to the surface potential from the surface charge outside the contact region. The integral are those from the surface charges in the contact region. Theprefactor is \( \frac{1}{2\pi} \) (instead of \( \frac{1}{4\pi} \)) because of the well-known jump condition for surface potentials.\(^{12}\) The distance at denominator is approximated using that for the flat surface, which leads to negligible error because only the contact region is of concern. The upper bound is set to infinity for convenience, as we shall see below, the singular surface charge density dies off rapidly outside the contact region.

The surface charge density \( \sigma_i(r) \) in eq. (2) are related to the potential difference, \( \Delta V(r) \equiv \phi_1(r) - \phi_2(r) \). By analogy to the conductor case, the electric field is approximately vertical and its magnitude is \( \Delta V(r)/(h + r^2/a) \). Then applying Gauss’s law, we get the charge density on the top surface

\[
\sigma_1(r) = \epsilon_0 \left( 1 - \epsilon_{r,1}^{-1} \right) \frac{\Delta V(r)}{h + r^2/a}, \] (3)

where \( \epsilon_{r,1} \equiv \epsilon_1/\epsilon_0 \). The charge density \( \sigma_2 \) is given similarly, but with a negative sign. Substituting the charge densities to eq. (2) and taking the difference gives an integral equation for \( \Delta V(r) \). The dependence on the unknown, \( \hat{V}_1 - \hat{V}_2 \), can be factored out by introducing an auxiliary, \( f(r) \equiv 1 - \Delta V(r)/(\hat{V}_1 - \hat{V}_2) \), which satisfies

\[
f(r) = \frac{\epsilon_{r,1}^{-1} + \epsilon_{r,2}^{-1}}{2\pi} \int_0^{\infty} dr' \frac{1}{h + r'^2/a} \frac{4r'}{r + r'} K(x). \] (4)

Here the integral over the azimuthal angle has been replaced with the complete elliptic function of the first kind \( K(x) \), where \( x \equiv \frac{r^2}{(r + r')^2} \). When \( \epsilon_1 = \epsilon_2 \), eq. (3) reduces to Batchelor’s original result, eq. (4.5) in ref. 16. Since \( f(r) \) is proportional to the contribution from the surface charges in the contact region, we see that it is dominated by particles of lower permittivity. When both permittivities approach infinity, we have \( f(r) = 0 \) and \( \Delta V(r) = \hat{V}_1 - \hat{V}_2 \), which
is identical to the expression for the conductors discussed above. More general cases are discussed below.

The solution to eq. (11) is uniquely determined by the normalized distance $h/a$ and the average permittivity, $\epsilon_s = 2/(\epsilon_{r1}^{-1} + \epsilon_{r2}^{-1})$. As shown by Batchelor, eq. (11) can be non-dimensionalized to

$$f(\rho) = \frac{1}{\pi} \int_0^\infty \frac{d\rho^{'}}{\lambda + \rho^{'2}} \frac{4\rho^{'}}{\rho^{'2}} K(x)$$

in which $\rho \equiv r\epsilon_r/a$ and $\lambda \equiv h\epsilon_r^2/a$. The numerically solved $f(\rho)$ for a few representative $\lambda$ values are shown in Fig. 2a. For large gap distance, with $\lambda \gg 1$, $f(\rho)$ is nearly uniform, as expected. For smaller $\lambda$ values, $f(\rho)$ decreases from $f(0)$ with $r$ monotonically. The difference in electric potential at the contact points is proportional to $1 - f(0)$. The value of $f(0)$ increases as $h$ decreases, and reaches unity at $h = 0$, ensuring that the surface potential is continuous at the contact point. The variation of $f(\rho)$ obtained from the above local analysis is confirmed by directly solving the full potential distribution for dielectric dimers (inset, Fig. 2a).

Similar to eq. (1) for the conductor case, the singular part of surface charges on particle 1 is given, with $R_0$ being the regularizing cutoff of order $a$, by

$$Q_{s,1} = \frac{(V_1 - V_2)_{\text{out}}}{4\pi} \left(1 - \epsilon_{r1}^{-1}\right) \int_{r_1}^{R_0} 2\pi r \frac{[1 - f(r)]}{h + r^2/a}$$

The dependence on the dielectric permittivity appears in the prefactor $1 - 1/\epsilon_{r1}$ and in $f(r)$. The singular surface charge $Q_{s,2}$ on the particle 2 is given analogously, but with a negative sign. However, because of the dependence on the dielectric permittivity, $Q_{s,2}$ and $Q_{s,1}$ do not add up to zero. The first term in the square bracket gives the same $\ln(a/h)$ singular contributions as eq. (1). The second term represents the correction due to dielectric screening.

The singular capacitance defined by $c_1(h) \equiv Q_{s,1}/(V_1 - V_2)$ also has these two contributions. In the non-dimensionalized form, it reads

$$c_1(h) = \frac{1 - \epsilon_{r1}^{-1}}{4} \ln \frac{a}{h} - P(\lambda),$$

$$P(\lambda) \equiv \int_0^\infty d\rho \frac{2\rho}{\lambda + \rho^2} f(\rho).$$

In the last term, the upper bound is set to infinity because $f(\rho)$ decays rapidly (as $\ln \rho/\rho$, ref. [16]). The dielectric correction is contained in the term $P(\lambda)$, which depends on permittivity $\epsilon_r$ and relative gap distance $h/a$ through the combination $\lambda = h\epsilon_r^2/a$. The behavior of $P(\lambda)$ is derived from that of $f(\rho)$. For $\lambda \gg 1$, $P(\lambda)$ is vanishingly small, so the capacitance is dominated by $\ln(a/h)$, the characteristic behavior of conductors. On the other hand, when $\lambda \rightarrow 0$, the leading contribution to $P(\lambda)$ is $-\ln \lambda$, which cancels exactly the $\ln(a/h)$ dependence, leaving a term $2\ln \epsilon_r$ that diverges instead with the average permittivity. Further, we note that $c_1(h)$ approaches the conductor limit for $\epsilon_r \gg 1$.

The difference in contact charges between dielectric and conductor cases is solely contained in $P(\lambda)$. For intermediate separation, $c_1(h)$ shows a singular $\ln(a/h)$ dependence that is similar to the conductor behavior. However, as long as $\epsilon_r$ is finite, this logarithmic behavior will eventually be cut off by contribution from $P(\lambda)$ at sufficiently small separation. Therefore, unlike the conductor case, the contact capacitance for dielectrics is finite at $h = 0$. Instead, it approaches a constant proportional to $2\ln \epsilon_r$. Physically, the logarithmic $h$-dependence originates from the accumulated polarization charges at the interface. It is cut off for dielectrics because the potential difference, which gives rise to the polarization charge, is self-consistently determined by the latter. The weaker polarization effect for dielectrics eventually can not keep up with the needed potential difference for producing the polarization charge. The variation of $c_1(h)$ on $h$ and $\epsilon_r$ are shown in Fig. 2b. The crossover can be estimated by setting $\lambda = h\epsilon_r^2/a = 1$. The logarithmic divergence, although being cut at small gap separation, still plagues numerical calculations in practice.

Figure 2: (a) Variation of surface potential $f(\rho)$ along the radial direction for $\lambda = 0.0, 0.5, 1.0, 10.0, 1000$. The inset shows the normalized potential difference for spherical dimer with a minimum separation $h = 0.1a$ and parameters $(Q_s, \epsilon_r, a_i)$: $(1, 100, 1)$ and $(-1, 10, 2)$. Dots are numerically solved by a spectral method in bispherical coordinate and the solid line is proportional to $1 - f(r)$. (b) The singular capacitance $c_1$ is presented as a function of normalized surface separation $h/a$ and relative permittivity $\epsilon_r$. This type of crossover behavior has been confirmed in a study on dielectric spherical dimers using the image method. The limiting value of the capacitance $2\ln \epsilon_r$ as well as the crossover is also consistent with the analytically known result between a conducting sphere and a dielectric.
plane. However, unlike these two work on dimer particles, Batchelor’s result is strictly local, suggesting that the same type of singularity as represented by eq. (7) is applicable to all contact region in cluster of multiple dielectric particles, irrespective of the particle shape. In the following, we show that, the approach for isolating the singularity for contact between conductors can be generalized to treat the dielectric clusters, yielding the exact contact energy and distance-dependence with modest numerical cost.

We consider the cluster consisting of \( n \) dielectric spheres. Given the free charge distribution \( \rho_c(r) \), the potential \( \phi \) is governed by Poisson’s equation \( \nabla \cdot \epsilon(r) \nabla \phi = -\rho_c(r)/\epsilon_{\text{out}}, \) where \( \epsilon_{\text{out}} \) is the medium permittivity. The (relative) material permittivity \( \epsilon(r) \) is set to \( \epsilon_t \equiv \epsilon_{\text{in}}/\epsilon_{\text{out}} \) inside particles and unity in the medium. Although the general charge distribution poses no added difficulty, for simplicity, we focus on the case when only the free surface charge \( \sigma_t \) are present. In such case, the system energy can be written as surface integrals of the product of the free surface charge and the surface potential over all surfaces. Furthermore, when the surface charge distribution is uniform, the energy reduces to the sum of the product of the total charge and the average surface potential. Therefore, we denote the set of net charges on particles by \( Q \), and the mean surface potentials \( V \). The net charges and the mean potentials are linearly related, i.e.,

\[
Q = CV,
\]

where \( C \) is an \( n \times n \) “capacitance array”. In this notation, the total energy can be expressed as \( E = \frac{1}{2}Q \cdot C^{-1} \cdot Q \). For convenience, the total energy \( E \) presented below is always normalized by the self-energy of a single isolated sphere with the radius \( a \) and a net charge \( q \), \( q^2/(8\pi\epsilon_{\text{out}}a) \). We note that this formulation applies to arbitrary particle shapes and cluster configurations. If the surface charge distribution is non-uniform or any external excitation exists, a multipole expansion of surface charge in terms of dipole, quadrupole etc. is needed. The constitutive relation eq. (8) and the quadratic expansion to energy can be generalized to include the contribution from these higher multipoles and external electric fields. For the purpose of demonstrating how the contact singularity is isolated, we focus on the case of the uniform surface charge distribution.

Our method for dielectrics is an extension to our earlier work on conductors. Because the conductors are equipotential, the mean potential is also the surface potential at every point on the surface. Since the capacitance \( C \) in eq. (5) contains two types of contributions, one type dominated by close contacts between neighboring particles, and the other type from the remaining interactions from all particles, we decompose the capacitance \( C \) as follows

\[
Q = (C \sigma + H)V.
\]

Here, \( C \sigma \) is the singular capacitance for conductors derived above (assuming that all gap distances are \( h \)). Since \( C \sigma \) becomes significant only for small gaps, the entries in the array \( L \) are nonvanishing only for closely neighboring particles. Specifically, if particle \( i \) and \( j \) form a close contact, we set the entries \( L_{ij} = L_{ji} = -1 \). The diagonal entry \( L_{ii} \) equals the number of close neighbors of the particle \( i \). All other entries of \( L \) are set to zero. The singular capacitance \( L \) as defined here is the same as the adjacency matrix representing the connectivity of clusters (see ref. 5 for explicit examples). In practice, for a given cluster configuration, we first numerically solve the full capacitance array \( C \) at finite but small \( h \) values, then subtract from \( C \) the singular term \( c_v(h)L \), to get the regular capacitance \( H \).

The dependence of this regular capacitance is then fitted to a straight line when \( h \) is small, allowing us to obtain the full \( h \)-dependence for the capacitance array \( C \) and, consequently, the full \( h \)-dependence of energy, down to \( h = 0 \).

Generalizing eq. (4) to dielectrics requires two nontrivial modifications. First, the decomposition in eq. (9) is valid because the potential of the conductors can be used to evaluate the contact potential difference. But dielectrics are not equipotential, and the surface potential at the contact points \( \hat{V}_i \) generally differ from the average potential \( V_i \) by a numerical factor that depends on the dielectric permittivity and the cluster configuration. Its variation with gap distance \( h \) is weak, and approaches a constant as \( h \to 0 \). So we generalize eq. (9) to

\[
Q = (\hat{L} + H)V, \quad \hat{L}_{ij} = \frac{1}{V_j} \left\{ \begin{array}{ll}
\hat{V}_j^{(i)} & i \neq j; \\
\sum_{k=1}^N \hat{V}_j^{(k)} c_{jk} & i = j.
\end{array} \right.
\]

Above, the superscript ‘(i)’ in \( \hat{V}_j^{(i)} \) indicates that the contact potential is evaluated on the particle \( j \) at the contact formed with the particle \( i \). The singular capacitance \( c_{ij} \) is given from eq. (7) by \( c_{ij} = \frac{e_{\text{out}}}{\epsilon_{\text{out}}} \left( \ln \frac{a_{ij}}{a} - P(\lambda_{ij}) \right) \), which depends on the mean radius of curvature \( a \), gap distance \( h \), and \( \lambda \) value evaluated for the particle pair \( i \) and \( j \). From the definition, it is clear that \( \hat{L} \) is generally not symmetric, which however reduces to the (symmetric) form identical to eq. (9) in the conductor limit, since \( \hat{V}_j^{(i)} = V_j \) for all contacts on the particle \( j \).

Second, it turns out that the contact potentials exhibit strong dependence on the second order and more distant neighbors, because the dielectric screening is comparatively weak (see Fig. 4 below). Therefore, to ensure rapid convergence of the correct contact potentials, our construction of the adjacency array \( \hat{L} \) contains all pairs of particles. Fortunately, as we shall see below, this construction requires no extra computation other than evaluating the surface potentials at additional contact points.

In order to identify the regular part \( H \) using eq. (10), we numerically compute the full capacitance matrix \( C(h) \) and all the contact potentials \( \hat{V}_j^{(i)} \), for a range of small but nonzero \( h \) values. We used the boundary element method (BEM) implemented in the package COPSS to solve Poisson’s equation. The solution is expressed in terms of the induced bound (polarization) charges \( \sigma_b \), which satisfies the
following boundary integral equation,
\[
\frac{1 + \epsilon_\ell}{2} \sigma_b + (1 - \epsilon_\ell)\epsilon_{\text{out}} (\mathbf{E}_b + \mathbf{E}_\ell) \cdot \hat{n} = \frac{1 - \epsilon_\ell}{2} \sigma_f. \tag{11}
\]

Above, the electric field strength at the surface due to induced bound charge \(\sigma_b\) and free charges \(\sigma_f\) are expressed as surface integrals \((\alpha = b, f)\),
\[
\mathbf{E}_\alpha = \frac{1}{4\pi \epsilon_{\text{out}}} \int dS' \frac{r - r'}{|r - r'|^3} \sigma_\alpha(r'). \tag{12}
\]

By our convention, the surface normal \(\hat{n}\) points outward. For clusters of multiple particles, it is understood that different particles may have different values of permittivity \(\epsilon_\ell\). Equation (11) is linear in \(\sigma_b\) and \(\sigma_f\). After discretization, the bound charge is obtained by inverting the coefficient array. The apparent divergent diagonal entries while discretizing the surface integral eq. (12) can be re-parameterized to reproduce the correct self-energy. Further numerical details can be found in ref. 8. In all calculations by BEM presented in this work (the dimer example used the exact series expansion), we meshed each spherical surface into 17342 triangular patches such that mesh size is about 0.03 \(a\).

In general, for a cluster of \(n\) particles, \(n\) separate numerical calculations with \(n\) independent charge vectors \(\mathbf{Q}\) are needed to determine the full capacitance matrix \(\mathbf{C}\). The computational cost can be reduced by imposing the symmetry of the cluster configuration. Subtracting from \(\mathbf{C}\) the singular contribution \(\mathbf{L}\) is expected to give the \(h\)-dependence of the regular part \(\mathbf{H}\). However, unlike the conductor case, where the coefficient to the logarithmic term is exactly known, the singular capacitance \(\mathbf{L}\) for dielectrics depends on the calculated contact potentials \(V_j^{(i)}\), which is susceptible to the numerical precision and what is meant by ‘contact point’ on a surface mesh. In practice, we vary the gap distance \(h\) and compute a few trial values of contact potentials, then select the one that ensures the difference \(H_{ij}(h) = C_{ij} - \tilde{L}_{ij}\) converges linearly with \(h\) as \(h \rightarrow 0\) for all the entries. In the following, three examples are presented to demonstrate the nature of the contact singularity, and to show that the regularization scheme allows us to obtain the energy of cluster of dielectric particles with small \(h\).

The first example is a dimer of identical dielectric spheres. It is the simplest example for demonstrating the effects of interfacial polarization.\(^{6,9,10,21}\) Except a study on the interaction between a conducting sphere and a dielectric plane,\(^{22}\) very few past work tried to evaluate the energy at small separation, presumably due to the difficulty of resolving the aforementioned contact singularity. Therefore, we analyzed the polarization effect for dielectric dimers in close contact, verified the singular behavior in eq. (7), and showed that eq. (11) yields the full \(h\)-dependence of energy. We studied both symmetric \((\mathbf{Q} = (q, q))\) and asymmetric \((\mathbf{Q} = (q, -q))\) cases, for a range of permittivity values \((1 \leq \epsilon_\ell \leq 10^5)\). The energy at \(h = 0\) is presented as a function of relative permittivity, which agrees with the exact result (see SI) found using the tangent-sphere coordinate.

Figure 3: Electrostatic energy of a pair of identical spheres. (a) and (b): asymmetric charge \(\mathbf{Q} = (q, -q)\). (c) and (d): symmetric charge \(\mathbf{Q} = (q, q)\). In (b) and (d), dots are numerical results obtained using our proposed method, and curves are exact prediction obtained using the tangent-sphere coordinate (SI).

For the asymmetric case, interfacial polarization enhances the inter-particle attraction. To illustrate this effect, we subtract the energy of two isolated spheres from that of a dimer, then plot it against the gap distance in Fig. 3, for three representative values of \(\epsilon_\ell\): 10, \(10^2\) and \(10^4\). In absence of the polarization effect, the energy curves would exhibit no dependence on \(\epsilon_\ell\), and appear flat over this narrow range of \(h/a\) values. As \(\epsilon_\ell\) is increased from 1, we confirm the expected, stronger distance dependence, as \(h \rightarrow 0\). In particular, for the case of \(\epsilon_\ell = 10^4\), an apparent logarithmic dependence on \(h\) is seen in Fig. 3b, which is precisely the singularity revealed in eq. (7) and is stronger for higher permittivity values. On the other hand, when the permittivity \(\epsilon_\ell\) is decreased, this logarithmic dependence is cut off at an increasingly larger separation and becomes almost invisible when \(\epsilon_\ell = 1\).

The normalized energy difference, as shown in Fig. 3a, evaluated at \(h = 0\), is show in Fig. 3d for different \(\epsilon_\ell\) values. This contact energy represents the energy gain for bringing two particles from infinity to contact. In terms of the normalizing energy unit, \(q^2/(8\pi\epsilon_{\text{out}}a)\), its value is \(-1\) without the polarization effect, and becomes more negative as \(\epsilon_\ell\) increases, eventually reaching \(-2\) at \(\epsilon_\ell = \infty\).\(^{23}\) The contribution from the polarization effect for \(\epsilon_\ell \geq 100\) is comparable to the coulombic attraction alone. Moreover, we notice a slow convergence of contact energy for permittivities \(\epsilon_\ell \geq 10^3\), owing to the weak \(\ln \epsilon_\ell^2\) dependence in the contact capacitance eq. (7) at \(h = 0\). Finally, we affirm our results obtained from eq. (10), by comparing the contact energies to the exact analytical results (SI).

For the symmetric case, the interfacial polarization weakens the inter-particle repulsion, which is seen from the \(h\)-dependence of dimer energy. However, by symmetry, the potential difference in the gap region vanishes and thus no logarithmic behavior is observed in Fig. 3b. The energy scales linearly with \(h\) and a straightforward extrapolation
gives the contact energy for all permittivity values plotted in Fig. S3. A much weaker polarization effect is found. Even for the conductor case, only about 10% contact energy can be attributed to polarization effects. The contact energies converge for \( \epsilon_r \gtrsim 100 \), and reach \( 2(1/\ln 2 - 1) \approx 0.88 \), in agreement with Maxwell’s result\(^2\) for the conducting dimers. As for the asymmetric case, the full \( \epsilon_r \)-dependence matches the analytical calculation (SI). To conclude this example, we note that the symmetric case is a peculiar example where the contact singularity is strictly absent. For all other charge ratios, using the decomposition in eq. (10) to isolate the strong \( h \)-dependence is necessary.

The second example concerns the energy of 8 identical spheres placed at the vertices of a cube, which illustrates the importance of the second order contact for dielectric clusters. As discussed above, the singular capacitance \( L \) in eq. (10) contains not only contributions from the nearest neighbors, but also those from the second-order and higher order neighbors. Therefore, a sphere at a vertex of a cube forms a secondary contact with its 3 plane diagonal vertices, and a third order contact with the body diagonal vertex. Even though the higher order contributions are minor, because at such large separation, these contacts cease to be singular, keeping the second order contribution is essential for obtaining the correct linear scaling of the regular capacitance with gap distance \( h \) shown in Fig. 4a.

As in the dimer case, these regularized capacitance allow us to evaluate the energy at arbitrarily small gap distance. Figure 3d shows the normalized energies when only one particle is charged, for which all the energetic contributions come from the interfacial polarization. Comparing the results from BEM and our regularization schemes containing varying order of contact contributions, it is clear that keeping the higher order singular contribution is necessary for correctly evaluating the energy for \( h/a \lesssim 0.05 \). In contrast, no such terms are needed for the conducting case.

The third example is our main result on the energy of clusters, from which the cohesive energy is obtained by subtracting the self-energy of particles at infinite separation. We considered two limiting configurations: the most extended one with all spheres arranged along a straight line (string), and the most compact one with all spheres posited at the vertices of the platonic solids (polyhedron). In our earlier work on the conducting spheres, the charges are allowed to flow freely between contacting spheres. The energy of polyhedron packing is found to be lower than that of the string packing at a finite separation. However, as the gap distance decreases, the polarization effects due to contact singularity become increasingly relevant, which ultimately makes the string packing to be energetically more favorable than the polyhedron packing. For the dielectric cases, we show that the weakened contact singularity causes another crossover between the relative stability of string-like and polyhedral packings.

As the previous example, to highlight the polarization effects, a unit charge \( q \) is placed on one sphere. For symmetric polyhedron packing, this charged sphere is arbitrarily chosen. For the string packing, we considered two extreme placings: at one end (string-1) and in the middle (string-2). For each particle configuration and charge assignment, we considered two scenarios: charge transfer between contacting particles is permitted (Fig. 4b) and prohibited (Fig. 4a).

When inter-particle charge transfer is permitted, while maintaining uniform charge distribution on each individual particle, the energy \( E \) can be calculated using \( Q \cdot C^{-1} \cdot Q/2 \). Minimizing this energy subject to the constraint of constant total charge \( q \), the optimal charge assignment is found to be \( Q_c = q C \cdot u/C_c \), where \( u \equiv (1, 1, \ldots, 1) \) and \( C_c \equiv \sum_{i,j=1}^n C_{ij} \). This implies that the optimal charge \( Q_c \) produces identical average surface potentials for all the particles, which generalizes the ‘equipotential’ concept for conductors. Correspondingly, the minimized energy is given by \( q^2/(2C_c) \), where the mean capacitance \( C_c \) weakly depends on the dielectric permittivity. In this scenario, there is no need to differentiate string-1 and string-2 configurations. The energies of string and polyhedron configurations at \( h = 0 \) are plotted in Fig. 4a, for \( \epsilon_r = 10 \) and 500. For all configurations, the energy decreases with the cluster size \( n \) monotonically since the redistributed surface charges are
The polarization effect is stronger. The energy of string is lower for the cluster with higher permittivity, because the energy for both string-1 and string-2 configurations saturate as the cluster size grows beyond $n = 12$, because the polarization effect is short-ranged. To assess the relative stability of compact or extended configurations, we then only need to focus on the string-2 and the polyhedron cases.

Our results indicate that the relative energetic stability depends on the permittivity. For $\epsilon_r = 10$, the energy of the polyhedron packing is lower than the string-2 packing, which is opposite to the characteristic result for conductors shown in Fig. 5a. Therefore, we expect a crossover from stable compact packing to stable open packing at intermediate permittivity values. This is indeed the case shown for $\epsilon_r = 500$, whereby the energies of compact and open configurations closely trace each other, and the relative energetic stability changes at $n = 4$ and $n = 8$ respectively. As $\epsilon_r$ is further increased, the energy curves of corresponding configuration will converge to those in Fig. 5a, reversing the relative stability of open and compact packings.

In summary, we generalized our previous work on conducting particles and developed a scheme to resolve the singular contact charges between touching dielectric spheres, which regularizes the full capacitance array by isolating the singular contributions, i.e., eq. (10). Using this scheme, we obtain the cohesive energies for dielectric clusters at zero separation containing up to $n = 20$ particles, which is difficult to resolve with brutal force numerical calculations. Our results show that the shape of stable clusters formed from dielectric particles depends on the permittivity ratio $\epsilon_r$: open clusters are more stable for large $\epsilon_r$, and compact clusters are more stable for small $\epsilon_r$. Our scheme is applicable to systems with arbitrary packing geometry, charge distribution, and containing asymmetric interfaces that have different permittivities and radii of curvature on the contacting particles. At the heart of our scheme is the contact singularity, which resembles those encountered in the study of thermal conduction and momentum transport across a narrow gap.

![Figure 5: Size dependence of electrostatic energy $\mathcal{E}$ for string-like and polyhedral configurations, with fixed total charge. (a) Charge transfer is permitted. Dashed curve: $\mathcal{E} = (2/n)^{1/3}/(2 \ln 2)$, the energy for polyhedral configurations of conducting spheres. Solid curve: $\mathcal{E} = \ln(2na/r_0)/[n \ln 2 \ln(2a/r_0)]$, the energy for a conducting cylinder of the same volume with length $L = 2na$ and radius $r_0 = 0.816 a$. (b) Charge transfer is prohibited. The total charge $q$ resides on the middle particle of the string (string-2) and an arbitrary vertex of polyhedron (polyhedron).](image-url)

Further apart. The dependence on permittivity is surprisingly weak, and the size-dependence is nearly indistinguishable from that of the conductor case. Two curves are obtained by treating the cluster as a single conductor respectively, whose capacitance scales with the length scale of the cluster, i.e., $n^{1/3}$ for the polyhedron packing and $n/\ln(n)$ for the string packing. The extended string packing has a lower cohesive energy because its effective capacitance is higher than that of the compact polyhedron packing.

More interesting behavior is found when charge transfer is prohibited. The dependence on permittivity is evident for all three cases: string-1, string-2, and polyhedron. To better visualize energies of string-2 and polyhedron packing, energies of string-1 is presented in Fig. S4) The energy is lower for the cluster with higher permittivity, because the polarization effect is stronger. The energy of string-2 is lower than that of string-1 for identical $n$, because the charged particles in the middle of the string can polarize the particles in two half strings. Further, the energies for both string-1 and string-2 configurations saturate as the cluster size grows beyond $n = 12$, because the polarization effect is short-ranged. To assess the relative stability of compact or extended configurations, we then only need to focus on the string-2 and the polyhedron cases.

Our results indicate that the relative energetic stability depends on the permittivity. For $\epsilon_r = 10$, the energy of the polyhedron packing is lower than the string-2 packing, which is opposite to the characteristic result for conductors shown in Fig. 5a. Therefore, we expect a crossover from stable compact packing to stable open packing at intermediate permittivity values. This is indeed the case shown for $\epsilon_r = 500$, whereby the energies of compact and open configurations closely trace each other, and the relative energetic stability changes at $n = 4$ and $n = 8$ respectively. As $\epsilon_r$ is further increased, the energy curves of corresponding configuration will converge to those in Fig. 5a, reversing the relative stability of open and compact packings.

In summary, we generalized our previous work on conducting particles and developed a scheme to resolve the singular contact charges between touching dielectric spheres, which regularizes the full capacitance array by isolating the singular contributions, i.e., eq. (10). Using this scheme, we obtain the cohesive energies for dielectric clusters at zero separation containing up to $n = 20$ particles, which is difficult to resolve with brutal force numerical calculations. Our results show that the shape of stable clusters formed from dielectric particles depends on the permittivity ratio $\epsilon_r$: open clusters are more stable for large $\epsilon_r$, and compact clusters are more stable for small $\epsilon_r$. Our scheme is applicable to systems with arbitrary packing geometry, charge distribution, and containing asymmetric interfaces that have different permittivities and radii of curvature on the contacting particles. At the heart of our scheme is the contact singularity, which resembles those encountered in the study of thermal conduction and momentum transport across a narrow gap.

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Exact polarization energy for clusters of contacting dielectrics

Supplementary information

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We provide a detailed derivation of a spectral method for the electrostatic problem of two touching dielectric spheres carrying uniform free surface charges in the tangent-sphere coordinates. The similar problem of touching dielectric spheres in presence of an electrostatic field has been solved by Pitkonen previously.\textsuperscript{4} We begin by introducing the tangent-sphere coordinates and review some useful mathematical facts about the Poisson’s equation in the tangent-sphere coordinates. We then provide a step-by-step derivation of the theory and illustrations of the method at the end.

First, we introduce the notation of the tangent-sphere coordinates by defining the transformation from the tangent-sphere coordinates \((\mu, \nu, \phi)\) to the Cartesian coordinates \((x, y, z)\)

\[ x = \frac{\mu \cos \varphi}{\mu^2 + \nu^2}, \quad y = \frac{\mu \sin \varphi}{\mu^2 + \nu^2}, \quad z = \frac{\nu}{\mu^2 + \nu^2}, \]  

(1)

where \(z\)-axis is the line connecting centers of two spheres. In this curvilinear coordinate,\textsuperscript{2} spherical surfaces tangent to \(xy\)-plane at the origin have constant \(\nu\) value in \(\nu \in (-\infty, +\infty)\). The value of \(\nu\) is determined by the radius of the spherical surface through \(\nu = \pm 1/(2a)\), where + and − indicate the surfaces with \(z > 0\) and \(z < 0\), respectively. \(\nu = 0\) denotes the \(xy\)-plane thereby. The surface of a circular toroid centered at origin without a hole, whose radius of circular section is \(\mu\), has a constant \(\mu\) value in \(\mu \in [0, +\infty)\). Lastly, \(\varphi \in [0, 2\pi]\) is the azimuth angle. The Euclidean distance \(d\) between points \((\mu, \nu, \varphi)\) and \((\mu', \nu', \varphi')\) is expressed as

\[ d = \left( \frac{\mu^2 - 2\mu\mu' \cos(\varphi - \varphi') + \mu'^2 + (\nu - \nu')^2}{(\mu^2 + \nu^2)(\mu'^2 + \nu'^2)} \right)^{1/2} \]

(2)

The electrostatic potential \(\phi\) is governed by the Poisson’s equation \(\nabla \cdot \epsilon(r) \nabla \phi(r) = -\rho(r)/\epsilon_0\), where \(\epsilon(r)\) and \(\epsilon_0\) are the relative permittivity and the vacuum permittivity, and \(\rho(r)\) is the free charge distribution. \(\rho(r)\) is nonzero only if \(r\) is on the surfaces in our problem setting. We denote \(\phi_i(i = 1, 2)\) as the potential inside the sphere \(i\) and \(\phi_0\) as the potential outside two spheres. Within each region, the potential \(\phi_i\) satisfies the Laplace’s equation \(\nabla^2 \phi_i = 0\) and then the solution \(\phi_i\) can be deduced from the general solution of Laplace’s equation in tangent-sphere coordinates by matching the values of \(\phi_i\) on boundaries.

The potential function \(\phi(\mu, \nu, \varphi)\) satisfying the Laplace’s equation in the tangent-sphere coordinates is \(R-\)separable\textsuperscript{2}, in which \(R(\mu, \nu) \equiv (\mu^2 + \nu^2)^{1/2}\), and has the following general form

\[ \phi(\mu, \nu, \varphi) = R(\mu, \nu) \int_0^\infty d\lambda \lambda J_n(\lambda \mu) \left( A_n(\lambda) e^{\lambda \nu} + B_n(\lambda) e^{-\lambda \nu} \right) \begin{bmatrix} \cos n \varphi \\ \sin n \varphi \end{bmatrix}. \]

(3)

Above, \(n\) takes nonnegative integers \(n = 0, 1, 2, \ldots\), \(J_n(x)\) is the \(n\)-th order Bessel function of the first kind. \(A_n(\lambda), B_n(\lambda)\) are two continuous spectra of \(\lambda\) that will be determined through matching boundary values. The integral above is the Hankel transform of order \(n\). The definition of Hankel transform of order \(n\) and its inverse transform are

\[ \Phi_n(\mu, \nu) = \int_0^\infty d\lambda \lambda J_n(\lambda \mu) \Phi(\lambda, \nu), \]

(4a)

\[ \Phi(\lambda, \nu) = \int_0^\infty d\mu \mu J_n(\lambda \mu) \Phi_n(\mu, \nu). \]

(4b)
Owing to the rotational symmetry of the dimer problem we concerned, we shall only need the solution with \( n = 0 \) and thus the \( \varphi \)-dependence can be dropped in our discussion below. We refer the further details about tangent-sphere coordinates to ref. 2.

We present below a step-by-step derivation of the spectral method for the case of asymmetric free charges \( Q = (q, -q) \). The other case of symmetric free charge \( Q = (q, q) \) is dealt in the identical procedure, whose final form of solution would be provided directly in parallel with that of the asymmetric case. To simplify the algebra, we consider the dimer of identical spheres with radius \( a_1 = a_2 = a = \frac{1}{2} \) and define the permittivity contrast \( \epsilon_r = \epsilon_{\text{in}} / \epsilon_{\text{out}} \), where \( \epsilon_{\text{in}} \) and \( \epsilon_{\text{out}} \) are the relative permittivities of the particles and the medium. The vacuum permittivity \( \epsilon_0 \) is set to the unity in below. The surfaces of two spheres then have the constant value \( \nu = \pm 1 \) in our convention and the centers of sphere are \((0, \pm 2, 0)\) in the tangent-sphere coordinates. For convenience, the potentials \( \phi \) and energies \( \xi \) shown below are always normalized by the self potential and self energy of a single isolated sphere in the vacuum, i.e. \( q/(4\pi\epsilon_0a) \) and \( q^2/(8\pi\epsilon_0a) \), respectively.

For the dimer with asymmetric free charges, the potentials has to be antisymmetric with respect to the \( xy \)-plane, i.e. \( \phi(\mu, \nu) = -\phi(\mu, -\nu) \). Therefore, we only need to consider the potential \( \phi_1 \) and \( \phi_0 \) in the upper half space \( \nu > 0 \). The potentials outside the sphere \( \phi_0 \) and inside the sphere \( \phi_1 \) are

\[
\begin{align*}
\phi_0(\mu, \nu) &= \frac{1}{\epsilon_{\text{out}}} \left( \frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu - 2)^2)^{1/2}} - \frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu + 2)^2)^{1/2}} \right) + \frac{1}{\epsilon_{\text{out}}} \psi_0(\mu, \nu), \\
\phi_1(\mu, \nu) &= \frac{1}{\epsilon_{\text{out}}} \left( 1 - \frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu + 2)^2)^{1/2}} \right) + \frac{1}{\epsilon_{\text{out}}} \psi_1(\mu, \nu).
\end{align*}
\]

Here, the first part of contribution in the parentheses come from the free charges of two spheres. The second part, potentials \( \psi_0 \) and \( \psi_1 \), represents the contribution from the induced bound charges. One can show that the first part satisfies the Laplace’s equation by themselves alone, which follows that the \( \psi_0 \) and \( \psi_1 \) do the same.

The potentials \( \psi_0 \) and \( \psi_1 \) generated by the induced bound charges can then be expressed in the form of eq. (3)

\[
\begin{align*}
\psi_0(\mu, \nu) &= R(\mu, \nu) \int_0^\infty d\lambda \lambda J_0(\lambda \mu) \left( 2 A^{(0)}(\lambda) \sinh \lambda \nu \right), \\
\psi_1(\mu, \nu) &= R(\mu, \nu) \int_0^\infty d\lambda \lambda J_0(\lambda \mu) \left( B^{(1)}(\lambda) e^{-\lambda \nu} \right).
\end{align*}
\]

The superscript ‘(i)’ of the spectra \( A^{(0)}(\lambda) \) and \( B^{(1)}(\lambda) \) denotes the region to which they belong. Outside the sphere, \( \psi_0(\mu, \nu) \) is an odd function with respect to \( \nu \) so that we have \( \psi_0(\mu, \nu) = -\psi_0(\mu, -\nu) \) and consequently \( A^{(0)}(\lambda) = -B^{(0)}(\lambda) \) resulting in eq. (6a). Inside the sphere, \( \psi_1(\mu, \nu) \) is finite everywhere including \( \nu = +\infty \) (\( \nu \to +\infty \) denotes the smallest spherical surface, which approaches the Cartesian origin within the sphere 1.) Therefore, \( A^{(1)}(\lambda) = 0 \) is necessary to keep the \( e^{\lambda \nu} \) from blowing up the integrand. Now, our object is to find the spectra \( A^{(0)}(\lambda) \) and \( B^{(1)}(\lambda) \) that match the boundary values of \( \phi_0 \) and \( \phi_1 \) on the interface \( \nu = 1 \).

Two spectra \( A^{(0)}(\lambda) \) and \( B^{(1)}(\lambda) \) are determined by the two boundary conditions on \( \nu = 1 \): (a) the continuity of potential across the boundary and (b) the discontinuity of normal component of electric field across the boundary, which equals to the free surface charge density required by Gauss’s law. Mathematically, we have

\[
\begin{align*}
\phi_0(\mu, 1_-) &= \phi_1(\mu, 1_+) \\
-(\mu^2 + \nu^2) \frac{\partial \phi_0}{\partial \nu} \bigg|_{\nu = 1_-} + \epsilon_r (\mu^2 + \nu^2) \frac{\partial \phi_1}{\partial \nu} \bigg|_{\nu = 1_+} &= \frac{1}{a} \qquad (7b)
\end{align*}
\]

The normal component of electric field on the surface \( \nu = 1 \) is \( |E| = -(\mu^2 + \nu^2) \frac{\partial \phi}{\partial \nu} \), pointing inward (outward) on \( \nu = 1 \) (\( \nu = -1 \)).

To obtain the equations for the spectra, we manipulate eq. (7a) and eq. (7b) in following steps: (1) Inserting eq. (5); (2) Dividing both sides by \( (\mu^2 + 1)^{1/2} \); (3) Applying Hankel transformation of the zeroth order to both sides. Equation (7a) is then transformed to

\[
2 A^{(0)}(\lambda) \sinh \lambda = B^{(1)}(\lambda) e^{-\lambda} \equiv C(\lambda) \qquad (8a)
\]

where \( C(\lambda) \) is an auxiliary function defined for convenience. With eq. (8a), two unknown spectra are effectively reduced to one. The normal boundary condition eq. (7b) is proceeded in the same way but dividing both sides by \( (\mu^2 + 1)^{3/2} \). In terms of \( C(\lambda) \), it becomes

\[
\int_0^\infty d\mu \frac{\mu J_0(\lambda \mu)}{\mu^2 + 1} \int_0^\infty d\tau J_0(\tau \mu) C(\tau) - \frac{\epsilon_r + \cot \lambda \theta}{\epsilon_r - 1} \lambda C(\lambda) = \int_0^\infty d\mu \frac{\mu J_0(\lambda \mu)}{(\mu^2 + 1)(\mu^2 + 9)^{1/2}} - (e^{-3\lambda} + 2e^{-\lambda}). \qquad (8b)
\]
Two useful Hankel transformations needed in our manipulation here are

\[
\int_0^\infty \frac{\mu J_0(\lambda \mu)J_0(\tau \mu)}{\mu^2 + 1} \, d\mu = e^{-\lambda \tau}/\lambda, \quad (9a)
\]
\[
\int_0^\infty \frac{\mu J_0(\lambda \mu)J_0(\tau \mu)}{\mu^2 + 9} \, d\mu = e^{-\lambda \tau}. \quad (9b)
\]

The integral involving two Bessel functions \( J_0 \) on LHS of eq. (9a) can be simplified by integrating over \( \mu \) first. The formula 6.541 in ref.2 provides us a clean result to it

\[
\int_0^\infty \frac{\mu J_0(\lambda \mu)J_0(\tau \mu)}{\mu^2 + 1} \, d\mu = \begin{cases} I_0(\lambda)K_0(\tau), & \lambda \leq \tau, \\ I_0(\lambda)K_0(\lambda), & \lambda > \tau. \end{cases} \quad (10)
\]

where \( I(x) \) and \( K(x) \) are modified Bessel functions of the first kind and second kind, respectively. On the RHS of eq. (9b) the integral can be simplified by inserting the inverse Hankel transform of \((\mu^2 + 9)^{-1/2}\) utilizing the eq. (10a) and changing the order of integration

\[
\int_0^\infty \frac{\mu J_0(\lambda \mu)J_0(\tau \mu)}{\mu^2 + 1}(\mu^2 + 9)^{1/2} \, d\mu = \int_0^\infty d\tau \int_0^\infty \frac{\mu J_0(\lambda \mu)J_0(\tau \mu)}{\mu^2 + 1} \, d\mu. \quad (11)
\]

The inner integral can be evaluated in terms of the modified Bessel functions again by eq. (10).

For future convenience, we define a new auxiliary function \( g(\lambda) \)

\[
g(\lambda) = \frac{\epsilon - 1 + \coth \lambda}{\epsilon - 1} \lambda C(\lambda). \quad (12)
\]

Combining with the above simplifications on the integrals, the integral equation of \( C(\lambda) \) eq. (8b) is eventually reduced to an integral equation of \( g(\lambda) \)

\[
g(\lambda) - K_0(\lambda) \int_0^\lambda d\tau \, I_0(\tau) \left( \frac{\epsilon - 1}{\epsilon + \coth \tau} g(\tau) - e^{-3\tau} \right) - I_0(\lambda) \int_\lambda^\infty d\tau K_0(\tau) \left( \frac{\epsilon - 1}{\epsilon + \coth \tau} g(\tau) - e^{-3\tau} \right) = (e^{-3\lambda} + 2e^{-\lambda}) \quad (13)
\]

The integral equation of \( g(\lambda) \) above is a Fredholm integral equation of the second kind. It can be solved by transforming it to a differential equation of \( g(\lambda) \) after differentiating eq. (13) with respect to \( \lambda \) twice. The first differentiation is carried out in the following steps: (1) Dividing both sides by \( K_0(\lambda) \); (2) Differentiating both sides with respect to \( \lambda \); (3) multiplying both sides by \( \lambda K_0^2(\lambda) \). Equation (13) becomes

\[
\lambda(K_0(\lambda)g'(\lambda) + K_1(\lambda)g(\lambda)) - \int_\lambda^\infty d\tau K_0(\tau) \left( \frac{\epsilon - 1}{\epsilon + \coth \tau} g(\tau) - e^{-3\tau} \right) = \lambda[-(3e^{-3\lambda} + 2e^{-\lambda})K_0 + (e^{-3\lambda} + 2e^{-\lambda})K_1] \quad (13.1)
\]

The recurrence relation \( K_0'(\lambda) = K_1(\lambda) \) and also the equivalence \( K_0^2 \left( \frac{d}{dK_0} \right)' = 1/\lambda \) have been used.

Another direct differentiation with respect to \( \lambda \) of eq. (13.1) will get rid of the integral by Leibniz integral rule and lead to an ODE of \( g(\lambda) \) for asymmetric free charges \( Q = (q, -q) \)

\[
(\lambda g')' + \left( \frac{\epsilon - 1}{\epsilon + \coth \lambda} - \lambda \right) g(\lambda) = (-2 + 8\lambda)e^{-3\lambda}, \quad (14)
\]

where another recurrence relation \( K_1'(\lambda) = -K_0(\lambda) - K_1(\lambda)/\lambda \) has been used and two boundary conditions are derived through examining the behavior of \( g(\lambda) \) for \( \lambda = 0 \) and \( \lambda \to \infty \). Differentiating eq. (13) with respect to \( \lambda \) and evaluating it at the limit \( \lambda \to 0 \) will simply leave us with \( g'(0) = -5 \) as the derivatives of two integral expression with respect to \( \lambda \) in eq. (13) vanish at \( \lambda = 0 \). On the other hand, \( g(\infty) = 0 \) is necessary to ensure the integrability of eq. (8) when \( \mu = 0 \). Following the same procedure, we can derive another ODE of \( g(\lambda) \) and boundary conditions for the case of symmetric free charge \( Q = (q, q) \). Here, we save the repetitive algebra and simply present its final result

\[
(\lambda g')' + \left( \frac{\epsilon - 1}{\epsilon + \tanh \lambda} - \lambda \right) g(\lambda) = (-2 + 8\lambda)e^{-3\lambda}, \quad (15)
\]

\[
g'(0) = 5, \quad g(\infty) = 0.
\]
The major difference from eq. (14) is that the hyperbolic cotangent function in the denominator becomes the hyperbolic tangent function, reflecting the even symmetry of potential about the $xy$-plane. The solutions of $g(\lambda)$ for both cases with several representative values of $\epsilon_r$ are presented in Fig. (S1).

The contact energy that we are looking for is simply $E = \frac{1}{2} \sum_{i=1,2} Q_i V_i$ in our problem setting, where $V_i$ is the mean surface potential of sphere $i$. For spheres, the mean surface potential can be represented by the potential evaluated at its center due to the spherical symmetry. Therefore, we only need the potentials at $(0, \pm 2, 0)$ for the contact energies $E = \frac{1}{2} Q_1 \phi_1(0, 2, 0) + \frac{1}{2} Q_2 \phi_2(0, -2, 0)$, in which $\phi_i$ is calculated by eq. (3) with spectra found by solving respective ODE of $g(\lambda)$. The contact energies for the dimer of identical spheres are presented for both cases of symmetric charges and asymmetric charges with $\epsilon_r$ ranging from 0 to $\infty$ in Fig. (S2). The spectral method generalizes to dimer of spheres with different radii and permittivities immediately, and more importantly, to spheres with higher order multipole charges.

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Supplementary figures

Figure S1: The solutions of $g(\lambda)$ for both cases of asymmetric charges and symmetric charges with several representative values of $\varepsilon_r$ are presented. The solutions converge slowly in the asymmetric case due to the $\ln \varepsilon_r^2$ dependence of singular contact charges shown in the main text. On the other hand, the ones converge fast in the symmetric case. The solutions of $\varepsilon_r = 10$ and $\varepsilon_r = 10^2$ are almost indistinguishable for the case of symmetric charges.
Figure S2: The electrostatic energy of a touching pair of identical spheres for the case of asymmetric charges and symmetric charges. To emphasize the role of the electrostatic interaction, the energy of two isolated spheres, $E_{\text{self}}$ is subtracted from the total energy $E$. At $\epsilon_r = 1$, the polarization effect vanishes and thus the interaction is simply the coulombic interaction between two touching spheres, i.e. $-1$ and $1$, in the unit $q^2/(8\pi\epsilon_0a)$. When $\epsilon_r > 1$, the polarization effect enhances the attraction and makes the interaction energy approach $-2$ at the conducting limit $\epsilon_r \to \infty$. For the symmetric case, the interaction energy quickly converges to the known result, $2/\ln 2 - 2 \approx 0.88$. When $\epsilon_r < 1$, the polarization effect screens the coulombic interaction for both cases, which reduces the interaction energy to 0 at about $\epsilon_r \approx 10^{-2}$. 
Figure S3: The regular part $H_{ij}$ of capacitance coefficient $C_{ij}$ as a function of the normalized gap distance $h/a$. The indices of spheres are denoted in the sketch of the cube configuration. With respect to the sphere 1, sphere 2 is one of the nearest neighbor, sphere 5 is on one of the plane-diagonal vertices, and sphere 8 is on the body-diagonal vertex. The nonlinear behavior of $C_{ij}$ gradually diminishes for the pair of spheres forming only a secondary contact.

Figure S4: Size dependence of electrostatic energy $\mathcal{E}$ for string-like and polyhedron packing with fixed total charge, when charge transfer is prohibited. The total charge $q$ resides on one end of the string (string-1), the middle particle of the string (string-2), and an arbitrary vertex of polyhedron (polyhedron).