Electronic Supplementary Material (ESI) for Soft Matter.

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.[1] 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 (μ, ν, φ) to the Cartesian coordinates (x, y, z)

$$x = \frac{\mu \cos\varphi}{\mu^2+\nu^2}, \quad y = \frac{\mu \sin\varphi}{\mu^2+\nu^2}, \quad z = \frac{\nu}{\mu^2+\nu^2}. \tag{1}$$

where z-axis is the line connecting centers of two spheres. In this curvilinear coordinate,[2] spherical surfaces tangent to xy-plane at the origin have constant ν value in $\nu \in (-\infty, +\infty)$. The value of ν 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 μ, has a constant μ value in $\mu \in [0, +\infty)$. Lastly, $\varphi \in [0, 2\pi]$ is the azimuth angle. The Euclidean distance d between points (μ, ν, φ) and (μ', ν', φ') is expressed as

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

The electrostatic potential ϕ is governed by the Poisson's equation $\nabla \cdot \epsilon(\mathbf{r})\nabla\phi(\mathbf{r}) = -\rho_{\mathrm{f}}(\mathbf{r})/\epsilon_0$, where $\epsilon(\mathbf{r})$ and ϵ_0 are the relative permittivity and the vacuum permittivity, and $\rho_{\mathrm{f}}(\mathbf{r})$ is the free charge distribution. $\rho_{\mathrm{f}}(\mathbf{r})$ is nonzero only if $\mathbf{r}$ is on the surfaces in our problem setting. We denote $\phi_i (i = 1, 2)$ as the potential inside the sphere i and ϕ_0 as the potential outside two spheres. Within each region, the potential ϕ_i satisfies the Laplace's equation $\nabla^2\phi_i = 0$ and then the solution ϕ_i can be deduced from the general solution of Laplace's equation in tangent-sphere coordinates by matching the values of ϕ_i on boundaries.

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

$$\phi(\mu,\nu, \varphi) = R(\mu, \nu) \int_0^\infty \mathrm{d}\lambda\, \lambda J_n(\lambda\mu) \left(A_n(\lambda)e^{\lambda\nu} + B_n(\lambda)e^{-\lambda\nu} \right) \begin{Bmatrix} \cos n\varphi \\ \sin n\varphi \end{Bmatrix}. \tag{3}$$

Above, n takes nonnegative integrers $n = 0, 1, 2, \ldots$, $J_n(x)$ is the n-th order Bessel function of the first kind. $A_n(\lambda), B_n(\lambda)$ are two continuous spectra of λ 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

$$\Phi_n(\mu, \nu) = \int_0^\infty \mathrm{d}\lambda\, \lambda J_n(\lambda\mu)\overline{\Phi_n}(\lambda, \nu), \tag{4a}$$

$$\overline{\Phi_n}(\lambda, \nu) = \int_0^\infty \mathrm{d}\mu\, \mu J_n(\lambda\mu)\Phi_n(\mu, \nu). \tag{4b}$$

Owing to the rotational symmetry of the dimer problem we concerned, we shall only need the solution with $n = 0$ and thus the φ-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 $\mathbf{Q} = (q, -q)$. The other case of symmetric free charge $\mathbf{Q} = (q, q)$ 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 $\epsilon_{\mathrm{r}} = \epsilon_{\mathrm{in}}/\epsilon_{\mathrm{out}}$, where ϵ_{in} and ϵ_{out} are the relative permittivities of the particles and the medium. The vacuum permittivity ϵ_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 ϕ and energies $\mathcal{E}$ shown below are always normalized by the self potential and self energy of a single isolated sphere in the vacuum, i.e. $q/(4\pi\epsilon_0 a)$ and $q^2/(8\pi\epsilon_0 a)$, respectively.

For the dimer with asymmetric free charges, the potential 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 ϕ_1 and ϕ_0 in the upper half space $\nu > 0$. The potentials outside the sphere ϕ_0 and inside the sphere ϕ_1 are

$$\begin{aligned}
\phi_0(\mu, \nu) &= \frac{1}{\epsilon_{\mathrm{out}}} \left(\frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu - 2)^2)^{1/2}} - \frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu + 2)^2)^{1/2}} \right) + \frac{1}{\epsilon_{\mathrm{out}}} \psi_0(\mu, \nu), \\
\phi_1(\mu, \nu) &= \frac{1}{\epsilon_{\mathrm{out}}} \left(1 - \frac{(\mu^2 + \nu^2)^{1/2}}{(\mu^2 + (\nu + 2)^2)^{1/2}} \right) + \frac{1}{\epsilon_{\mathrm{out}}} \psi_1(\mu, \nu).
\end{aligned} \tag{5}$$

Here, the first part of contribution in the parenthesises come from the free charges of two spheres. The second part, potentials ψ_0 and ψ_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 ψ_0 and ψ_1 do the same.

The potentials ψ_0 and ψ_1 generated by the induced bound charges can then be expressed in the form of eq. (3)

$$\psi_0(\mu, \nu) = R(\mu, \nu) \int_0^\infty \mathrm{d}\lambda\, \lambda J_0(\lambda\mu) \left(2A^{(0)}(\lambda) \sinh \lambda\nu \right), \tag{6a}$$

$$\psi_1(\mu, \nu) = R(\mu, \nu) \int_0^\infty \mathrm{d}\lambda\, \lambda J_0(\lambda\mu) \left(B^{(1)}(\lambda) e^{-\lambda\nu} \right). \tag{6b}$$

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 ν 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 ϕ_0 and ϕ_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

$$\phi_0(\mu, 1_-) = \phi_1(\mu, 1_+) \tag{7a}$$

$$-(\mu^2 + \nu^2) \left. \frac{\partial \phi_0}{\partial \nu} \right|_{\nu = 1_-} + \epsilon_{\mathrm{r}} (\mu^2 + \nu^2) \left. \frac{\partial \phi_1}{\partial \nu} \right|_{\nu = 1_+} = \frac{1}{a}. \tag{7b}$$

The normal component of electric field on the surface ν 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

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

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

$$\int_0^\infty \mathrm{d}\mu\, \frac{\mu J_0(\lambda\mu)}{\mu^2 + 1} \int_0^\infty \mathrm{d}\tau\, \tau J_0(\tau\mu) C(\tau) - \frac{(\epsilon_{\mathrm{r}} + \coth \lambda)}{\epsilon_{\mathrm{r}} - 1} \lambda C(\lambda) = \int_0^\infty \mathrm{d}\mu\, \frac{\mu J_0(\lambda\mu)}{(\mu^2 + 1)(\mu^2 + 9)^{1/2}} - (e^{-3\lambda} + 2e^{-\lambda}). \tag{8b}$$

Two useful Hankel transformations needed in our manipulation here are

$$\int_0^\infty \mu \frac{\nu}{(\mu^2+\nu^2)^{1/2}} J_0(\lambda\mu)\mathrm{d}\mu = e^{-\lambda\nu}/\lambda, \tag{9a}$$

$$\int_0^\infty \mu \frac{\nu}{(\mu^2+\nu^2)^{3/2}} J_0(\lambda\mu)\mathrm{d}\mu = e^{-\lambda\nu}. \tag{9b}$$

The integral involving two Bessel functions J_0 on LHS of eq. (8b) can be simplified by integrating over μ first. The formula 6.541 in ref.[3] provides us a clean result to it

$$\int_0^\infty \mathrm{d}\mu \, \frac{\mu J_0(\lambda\mu) J_0(\tau\mu)}{\mu^2+1} = \begin{cases} I_0(\lambda)K_0(\tau), & \lambda \le \tau, \\ I_0(\tau)K_0(\lambda), & \lambda > \tau. \end{cases} \tag{10}$$

where $I(x)$ and $K(x)$ are modified Bessel functions of the first kind and second kind, respectively. On the RHS of eq. (8b), the integral can be simplied by inserting the inverse Hankel transform of $(\mu^2+9)^{-1/2}$ utlizing the eq. (9a) and changig the order of integration

$$\int_0^\infty \mathrm{d}\mu \, \frac{\mu J_0(\lambda\mu)}{(\mu^2+1)(\mu^2+9)^{1/2}} = \int_0^\infty \mathrm{d}\tau \, e^{-3\tau} \int_0^\infty \mathrm{d}\mu \, \frac{\mu J_0(\lambda\mu) J_0(\tau\mu)}{\mu^2+1}. \tag{11}$$

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 $g(\lambda)$

$$g(\lambda) \equiv \frac{\epsilon_\mathrm{r} + \coth\lambda}{\epsilon_\mathrm{r} - 1} \lambda C(\lambda). \tag{12}$$

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

$$g(\lambda) - K_0(\lambda) \int_0^\lambda \mathrm{d}\tau \, I_0(\tau) \left(\frac{\epsilon_\mathrm{r}-1}{\epsilon_\mathrm{r}+\coth\tau} g(\tau) - e^{-3\tau} \right) - I_0(\lambda) \int_\lambda^\infty \mathrm{d}\tau \, K_0(\tau) \left(\frac{\epsilon_\mathrm{r}-1}{\epsilon_\mathrm{r}+\coth\tau} g(\tau) - e^{-3\tau} \right) = (e^{-3\lambda} + 2e^{-\lambda}) \tag{13}$$

The integral equation of $g(\lambda)$ above is a Fredholm integral equation of the second kind. It can be solved by transforming it to an differential equatino of $g(\lambda)$ after differentiating eq. (13) with respect to λ 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 λ; (3) multiplying both sides by $\lambda K_0^2(\lambda)$. Equation˜(13) becomes

$$\lambda(K_0(\lambda)g'(\lambda) + K_1(\lambda)g(\lambda)) - \int_\lambda^\infty \mathrm{d}\tau \, K_0(\tau) \left(\frac{\epsilon_\mathrm{r}-1}{\epsilon_\mathrm{r}+\coth\tau} g(\tau) - e^{-3\tau} \right) = \lambda[-(3e^{-3\lambda} + 2e^{-\lambda})K_0 + (e^{-3\lambda} + 2e^{-\lambda})K_1] \tag{13.1}$$

The recurrence relation $K_0'(\lambda) = K_1(\lambda)$ and also the equivalence $K_0^2 \left(\frac{I_0}{K_0}\right)' = 1/\lambda$ have been used.

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

$$\begin{aligned} &(\lambda g')' + \left(\frac{\epsilon_\mathrm{r}-1}{\epsilon_\mathrm{r}+\coth\lambda} - \lambda \right) g(\lambda) = (-2+8\lambda)e^{-3\lambda}, \\ &g'(0) = -5, \quad g(\infty) = 0, \end{aligned} \tag{14}$$

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 λ 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 λ in eq. (13) vanish at $\lambda = 0$. On the other hand, $g(\infty) = 0$ is necessary to ensure the integrability of eq. (3) 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 $\mathbf{Q} = (q, q)$. Here, we save the repetitive algebra and simply present its final result

$$\begin{aligned} &(\lambda g')' + \left(\frac{\epsilon_\mathrm{r}-1}{\epsilon_\mathrm{r}+\tanh\lambda} - \lambda \right) g(\lambda) = -(-2+8\lambda)e^{-3\lambda}, \\ &g'(0) = 5, \quad g(\infty) = 0. \end{aligned} \tag{15}$$

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 ϵ_{r} are presented in Fig. (S1).

The contact energy that we are looking for is simply $\mathcal{E} = \frac{1}{2}\sum_{i=1,2} Q_i V_i$ 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 $\mathcal{E} = \frac{1}{2}Q_1\phi_1(0, 2, 0) + \frac{1}{2}Q_2\phi_2(0, -2, 0)$, in which ϕ_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 ϵ_{r} ranging from 0 to ∞ 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.

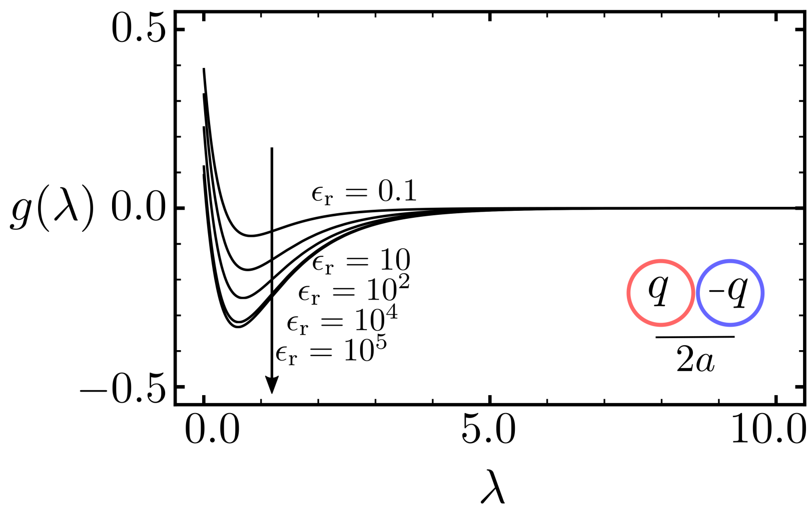
References

[1] M. Pitkonen. Polarizability of a pair of touching dielectric spheres. *J. Appl. Phys.*, 103(10):104910, 2008.

[2] P. Moon and D. E. Spencer. *Field Theory Handbook: including coordinate systems, differential equations and their solutions.* Springer, 2012.

[3] I. Solomonovich G. and I. Moiseevich R. *Table of Integrals, Series, and Products.* Academic press, 2014.

Supplementary figures



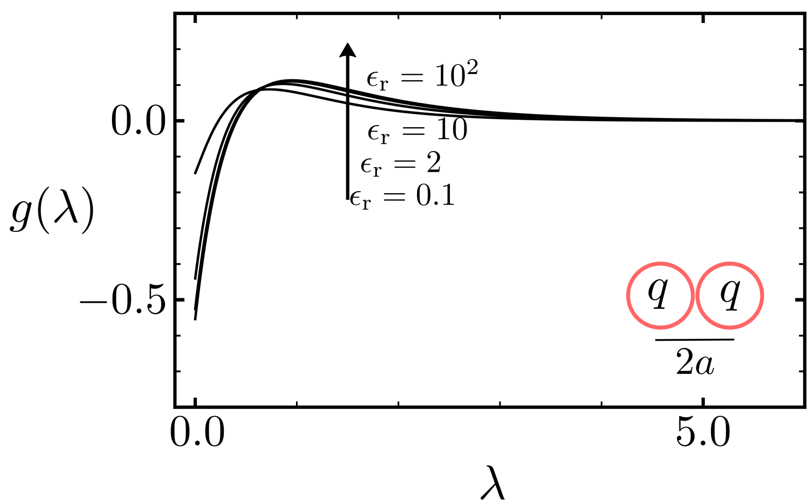


Figure S1: The solutions of $g(\lambda)$ for both cases of asymmetric charges and symmetric charges with several representative values of ϵ_r are presented. The solutions converge slowly in the asymmetric case due to the $\ln \epsilon_r^2$ dependence of singular contact charges shown in the main text. On the other hand, the ones converge fast in the symmetric case. The solutions of $\epsilon_r = 10$ and $\epsilon_r = 10^2$ are almost indistinguishable for the case of symmetric charges.

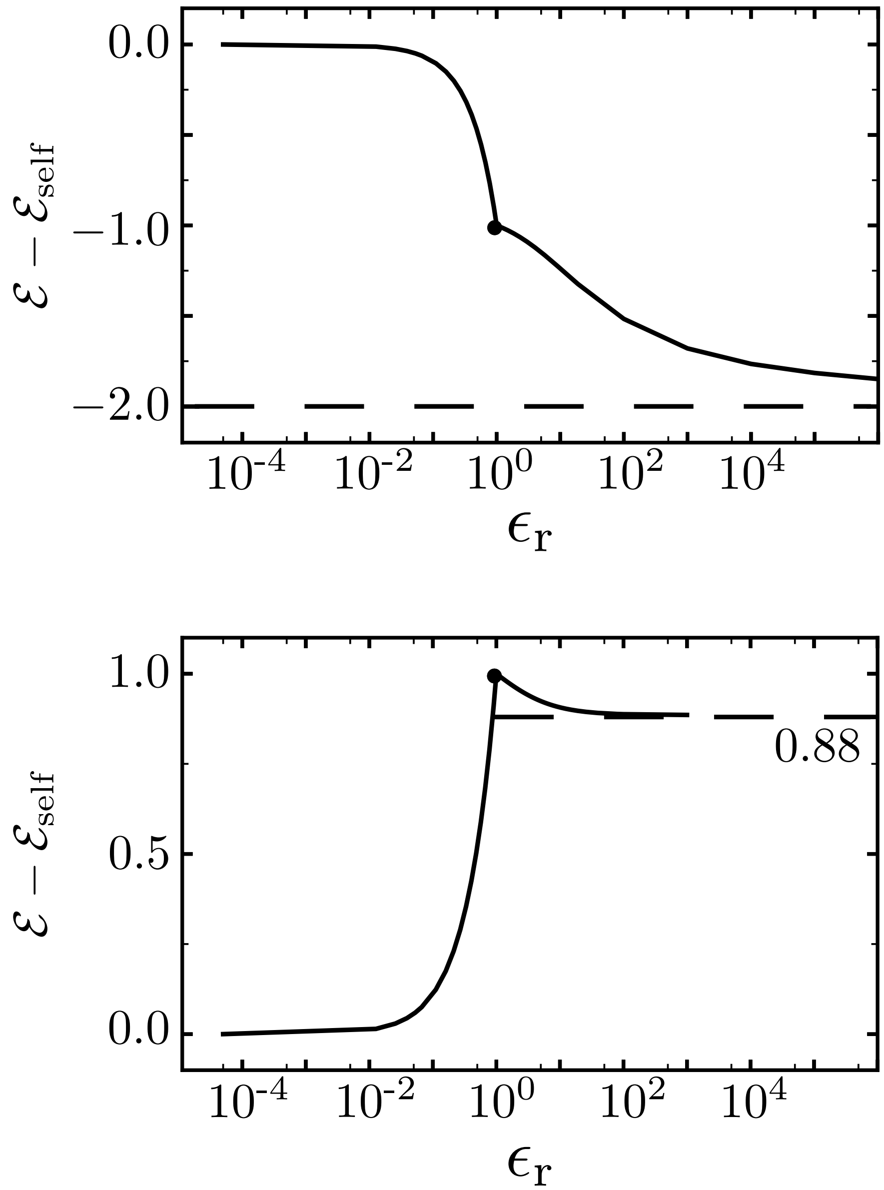


Figure S2: The electrostatic energy of a touching pair of identical spheres for the case of asymmetric charges and symmetric charges. To emphasize the role of the electrostatic interaction, the energy of two isolated spheres, $\mathcal{E}_{\mathrm{self}}$ is subtracted from the total energy $\mathcal{E}$. At $\epsilon_{\mathrm{r}} = 1$, the polarization effect vanishes and thus the interaction is simply the coulombic interaction between two touching spehres, i.e. -1 and 1, in the unit $q^2/(8\pi\epsilon_0 a)$. When $\epsilon_{\mathrm{r}} > 1$, the polarization effect enhances the attraction and makes the interaction energy approach -2 at the conducting limit $\epsilon_{\mathrm{r}} \to \infty$. For the symmetric case, the interaction energy quickly converges to the known result, $2/\ln 2 - 2 \approx 0.88$. When $\epsilon_{\mathrm{r}} < 1$, the polarization effect screens the coulombic interaction for both cases, which reduces the interaction energy to 0 at about $\epsilon_{\mathrm{r}} \approx 10^{-2}$.

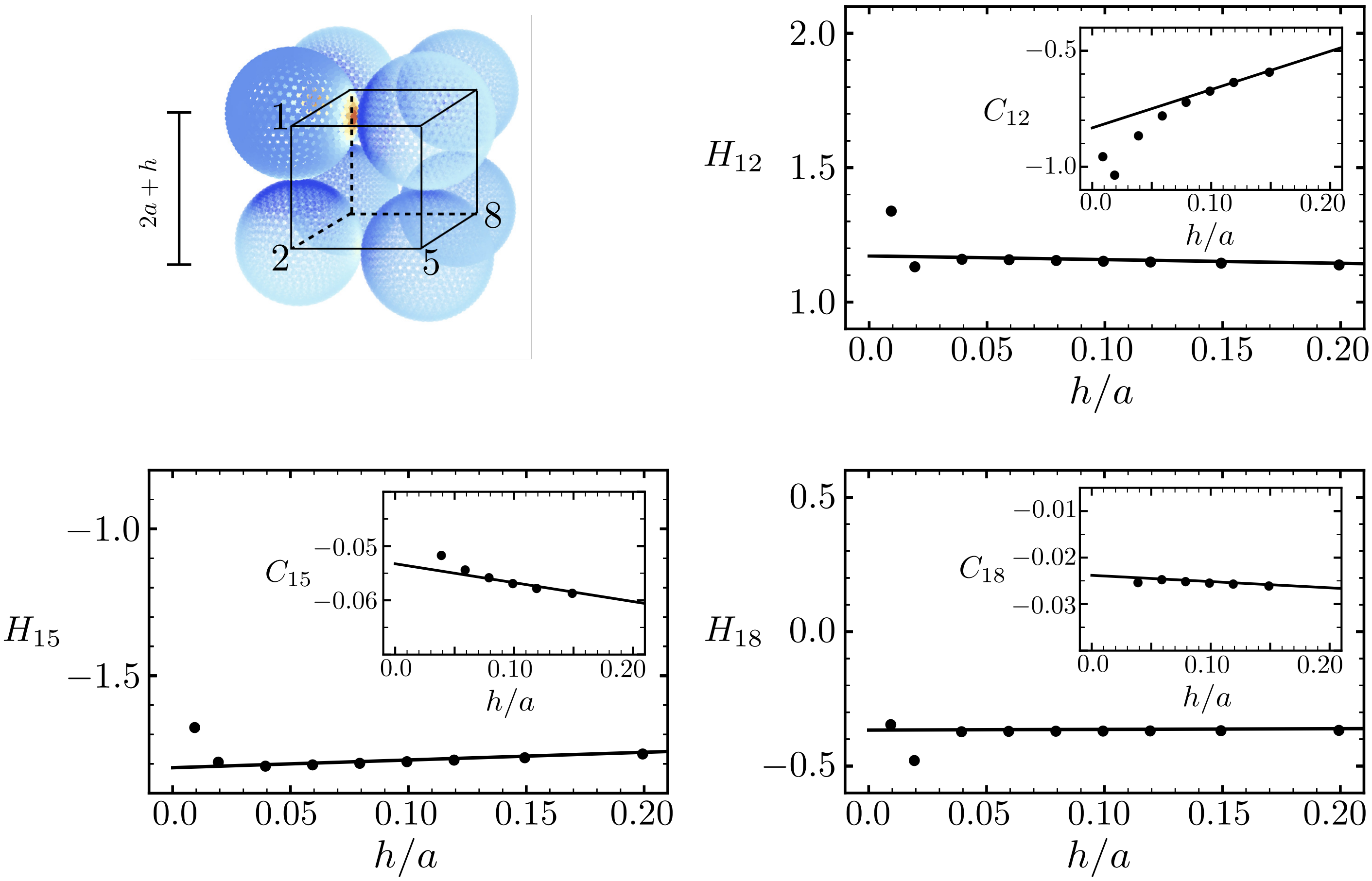


Figure S3: The regular part H_{ij} of capacitance coefficient C_{ij} as a function of the normalized gap distance h/a. The indices of spheres are denoted in the sketch of the cube configuration. With respect to the sphere 1, sphere 2 is one of the nearest neighbor, sphere 5 is on one of the plane-diagonal 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.

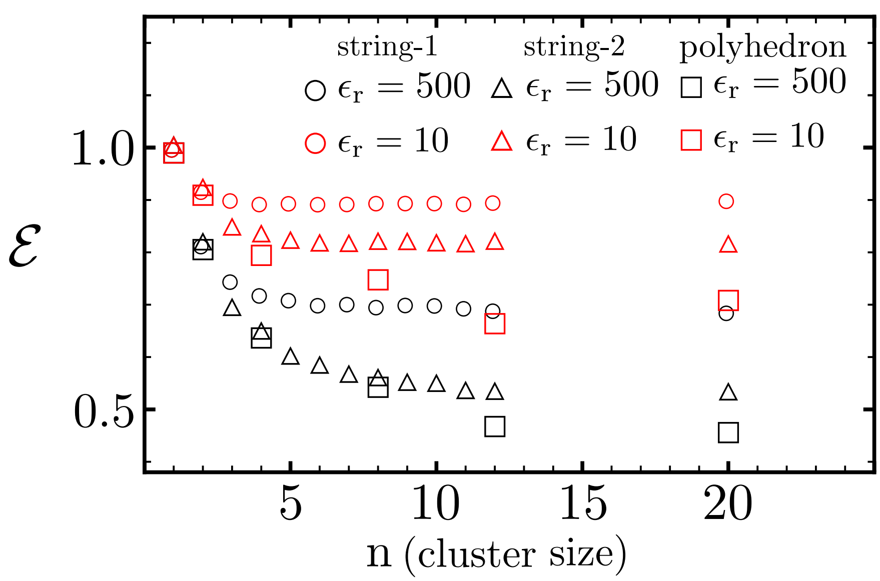


Figure S4: Size dependence of electrostatic energy $\mathcal{E}$ for string-like and polyhedron packing with fixed total charge, when charge transfer is prohibited. The total charge q resides on one end of the string (string-1), the middle particle of the string (string-2), and an arbitrary vertex of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