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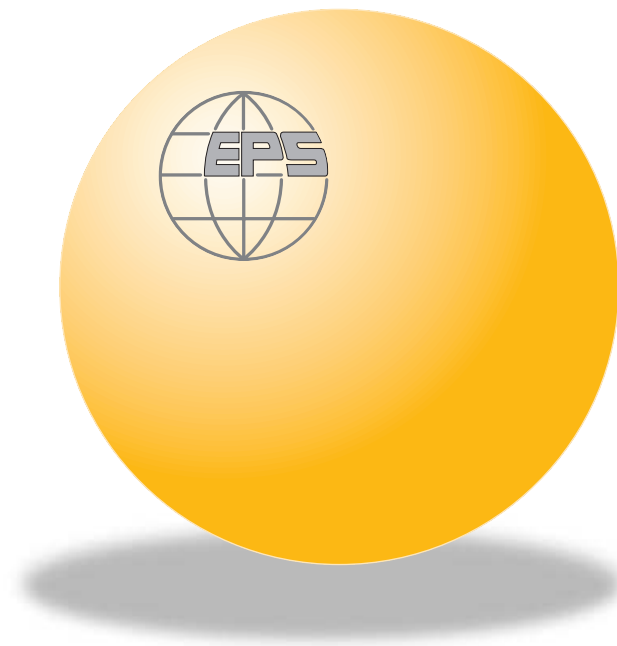
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## Electric forces among nanospheres in a dielectric host

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**Abstract.** – The force among a collection of dielectric spheres, suspended in a different dielectric host and subject to a uniform instantaneous external electric field, has been calculated as a function of the various parameters of the problem. A new approach is used to do this which is essentially exact: No assumptions are made regarding the smallness of spatial separation of neighboring spheres or the closeness of the two permittivities. In particular, the spheres can be metallic and the separation can be much smaller than the two radii. As an example, the case of two spheres is discussed in detail. Also discussed is the force acting on the smallest sphere in a nanolens configuration of three linearly aligned metallic spheres whose sizes and separations diminish consecutively in a self-similar fashion. Actually, the approach can be applied to find the force acting on any sphere in larger collections of spheres, subject to an external field which points in an arbitrary direction. Possible applications include simulations of electrorheological fluids.

Consider a suspension of high-dielectric-constant inclusions (often spherical in shape) in a host fluid of lower dielectric constant. When an electric field is applied, the inclusions become electrically polarized. The resulting forces between the inclusions then tend to make them line up in long chains. This chain-like structure dramatically increases the viscosity of the suspension. Such electrorheological fluids have found a variety of applications, *e.g.*, as electric-field-dependent lubricating fluids [1].

To calculate the properties of electrorheological fluids, it is important to know the forces acting on the suspended particles. These forces are mostly of two classes: electrostatic forces on the one hand, and dynamic forces arising from the presence of a moving fluid, such as viscous drag. Typically, the electrostatic forces are approximated as arising from two-body forces, which are due to the electric dipole moments induced in spheres [2–4]. However, when the separation between neighboring inclusion particles is small compared to their sizes,

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the dipole approximation (DA) breaks down and multipolar corrections, as well as many-body corrections, become important, even when the inclusions are spherical. This problem has typically been treated numerically, using numerical solutions of Laplace's equation [5] or finite-element techniques [6]. Notably, the DA may need further modification if the included particles have a finite conductivity [7]. An attempt to explicitly include forces due to higher-order-induced multipole moments was also made [8]. This led to complicated expressions which are apparently too cumbersome for use in dynamical calculations.

In this paper, we briefly describe a different and broadly applicable method for calculating the electrostatic forces acting on inclusions in a suspension. In contrast to some previous methods, this approach works for metallic as well as for dielectric spheres suspended in a dielectric fluid host. Furthermore, it goes beyond the dipole-dipole approximation and can include, in principle, all multipolar interactions. Finally, it does not assume that the interparticle interactions are a sum of two-body interactions, but instead treats them correctly as multipolar, many-body interactions. Our method is not restricted to suspensions of dielectric spheres in a dielectric host but can be applied even to conducting spheres. It can also be applied to ac fields in such a system even in the vicinity of a quasi-static resonance, where all the previously described methods fail.

The principle behind our approach is to note that the force  $\mathbf{F}_i$  acting on a suspended particle  $i$  is the negative gradient of the electrostatic energy  $W$  of the suspension with respect to the position  $\mathbf{r}_i$  of that particle:  $\mathbf{F}_i = -\partial W/\partial \mathbf{r}_i$ . The energy  $W$  is related to the local, instantaneous, real electric field  $\mathbf{E}(\mathbf{r})$  through

$$W \equiv \frac{1}{8\pi} \int_V \varepsilon(\mathbf{r}) \mathbf{E}^2(\mathbf{r}) dV, \quad (1)$$

where the local electric permittivity  $\varepsilon(\mathbf{r})$  is assumed to be real everywhere. Here we report on a method for calculating these forces which is based on the spectral representation for  $\mathbf{E}(\mathbf{r})$  and  $W$  [9]. In that representation, all quantities are expressed as sums of simple poles, which are the quasi-static resonances of the composite. These resonances can, in turn, be computed starting from the explicitly known quasi-static multipolar resonances of the individual spherical inclusions and certain overlap integrals between pairs of individual sphere eigenfunctions. We can thus obtain an explicit expression for  $W$  in terms of the eigenvalues and eigenvectors which characterize the quasi-static resonances of the composite. Those are easily computable, for arbitrary finite clusters of spherical inclusions, by numerical diagonalization of an exactly known matrix [10–13].

Besides the electrostatic energy, we are also able to obtain an explicit expression for the *force* on each suspended particle, in terms of this pole spectrum. This expression differs from previous dipolar results in two ways. First, it includes, in principle, all multipolar contributions to the forces. Secondly, the force is no longer a two-body force but includes contributions from three-body and many-body forces of higher order. Such forces are likely to be important in many geometries, especially when some of the suspended particles are nearly touching. These forces can, in principle, be used in a molecular-dynamics simulation of particle motion and aggregation in suspensions of dielectric spheres.

Here we present an explicit calculation of these forces for a few selected geometries. We consider two spheres with arbitrary (but equal) real dielectric constant  $\varepsilon_i$  embedded in a host with real dielectric constant  $\varepsilon_h$  (the restriction to real values of  $\varepsilon_i$ ,  $\varepsilon_h$  will be lifted in a forthcoming publication). The spheres may be of different radii. The calculation is valid even for  $\varepsilon_i \rightarrow \infty$ , as expected for a metallic sphere. As a simple illustration of the effects of three-body interactions, we consider a group of three spheres arranged in a straight line. We

show that there are substantial differences between the calculated forces on each sphere, and those which would be obtained in the two-body approximation where the forces are considered as the sum of two-body interactions.

When a single spherical inclusion of radius  $a$  is moved a small distance  $\delta z$  in the  $z$ -direction, the local electric field  $\mathbf{E}(\mathbf{r})$  changes by an  $\mathcal{O}(\delta z)$  amount in most locations. Due to the variational properties of eq. (1), such changes result in an  $\mathcal{O}[(\delta z)^2]$  change in the energy  $W$ , therefore the contribution to  $\mathbf{F}_i = -\nabla_i W$  is negligible. However, inside the  $\mathcal{O}(\delta z)$  infinitesimal change of the space occupied by the moved sphere the change in  $\mathbf{E}(\mathbf{r})$  is large. That change contributes an  $\mathcal{O}(\delta z)$  change to  $W$ . This change determines the force acting on the sphere along  $z$  as

$$\frac{8\pi}{a^2} F_z = \int \left[ (\varepsilon_i - \varepsilon_h) |\mathbf{E}|^2(\text{in}) + \frac{(\varepsilon_i - \varepsilon_h)^2}{\varepsilon_h} |E_r|^2(\text{in}) \right] \cos \theta \, d\Omega \quad (2)$$

$$= \int \left[ (\varepsilon_i - \varepsilon_h) |\mathbf{E}|^2(\text{out}) - \frac{(\varepsilon_i - \varepsilon_h)^2}{\varepsilon_h} |E_r|^2(\text{out}) \right] \cos \theta \, d\Omega, \quad (3)$$

where  $\theta$  and  $\Omega$  refer to polar angles around the center of the sphere, while  $E_r$  is the radial component of  $\mathbf{E}$ . The quantities  $\mathbf{E}(\text{in})$ ,  $E_r(\text{in})$  denote the field values just beneath the surface of the sphere, while  $\mathbf{E}(\text{out})$ ,  $E_r(\text{out})$  denote the field values just outside of that surface, and the integration over the entire solid angle means that only the field values at that surface are relevant for computing the force.

In order to compute the fields  $E_r(\text{in})$ ,  $E_r(\text{out})$  when a non-dilute collection of spherical inclusions is subject to an external uniform field  $\mathbf{E}_0 = E_0 \mathbf{e}_z$  along  $z$ , we exploit the spectral method, wherein the local potential field  $\phi(\mathbf{r})$  *inside the sphere* can be written in terms of the quasi-static resonances or eigenstates of that sphere, which are proportional to the regular spherical harmonic functions  $r^l Y_{lm}$ ,  $l \geq 1$  [10–12]:

$$\phi(\mathbf{r}) = \sum_{l \geq 1, m} b_{\mathbf{R}lm} \frac{r^l}{\sqrt{l} a^{l+1/2}} Y_{lm}(\Omega), \quad \text{for } \mathbf{r} \text{ inside the sphere centered at } \mathbf{R}. \quad (4)$$

The polar coordinates  $r$  and  $\Omega$  (*i.e.*, polar angle  $\theta$  and azimuth angle  $\varphi$ ) are defined relative to the sphere center. The expansion coefficients  $b_{\mathbf{R}lm}$  for  $\phi(\mathbf{r})$  inside the sphere centered at  $\mathbf{R}$  are determined from the eigenvalues  $s_n$  and the normalized-to-1 eigenvectors  $U_{\mathbf{R}lm}^{(n)}$  of the *entire collection of interacting spherical inclusions*:

$$b_{\mathbf{R}lm} = E_0 \sum_n \frac{s}{s - s_n} U_{\mathbf{R}lm}^{(n)} \langle U^{(n)} | z \rangle. \quad (5)$$

Here  $s$  is a physical parameter which is determined by the electric permittivities of the two constituents:

$$s \equiv \frac{\varepsilon_h}{\varepsilon_h - \varepsilon_i}, \quad (6)$$

while  $\langle U^{(n)} | z \rangle$  is the scalar product [11–13] of the two vectors  $U_{\mathbf{R}lm}^{(n)}$  and  $z_{\mathbf{R}lm} \equiv \sqrt{V_{\mathbf{R}}} \delta_{l1} \delta_{m0}$  ( $V_{\mathbf{R}} = 4\pi a_{\mathbf{R}}^3/3$  is the volume of the sphere centered at  $\mathbf{R}$ ; note that  $U_{\mathbf{R}l0}^{(n)}$  is real, even though  $U_{\mathbf{R}lm}^{(n)}$  is usually complex for nonzero values of  $m$ ):

$$\langle U^{(n)} | z \rangle \equiv \sum_{\mathbf{R}, l \geq 1, m} U_{\mathbf{R}lm}^{(n)*} z_{\mathbf{R}lm} = \sum_{\mathbf{R}} U_{\mathbf{R}10}^{(n)} \sqrt{V_{\mathbf{R}}}. \quad (7)$$

The eigenvalues  $s_n$  (which are special real values of  $s$ , all of them situated on the semi-closed real segment  $[0, 1)$ ) and eigenvectors  $U_{\mathbf{R}lm}^{(n)}$  (which are expansion coefficients of the quasi-static

resonances  $\phi_n(\mathbf{r})$  of the entire system in terms of all of the individual sphere eigenstates) are found by numerical solutions of a matrix eigenvalue problem, as described in refs. [11–13]. We note that  $\varepsilon_i, \varepsilon_h$  can be complex, in general, and consequently also  $s, \phi(\mathbf{r}), \mathbf{E}(\mathbf{r})$ , and  $W$ .

We first apply this procedure to configurations of (two or three) spheres aligned along the  $z$ -axis. Due to the axial symmetry of such configurations, the force on any sphere acts only in the  $z$ -direction. Furthermore, due to that symmetry, the eigenstates  $\phi_n(\mathbf{r})$ , which contribute to the potential field  $\phi(\mathbf{r})$  and hence to that force, are independent of the azimuth angle  $\varphi$ . Therefore, only the  $m = 0$  eigenstates of the individual spheres contribute to the eigenstates  $\phi_n(\mathbf{r})$ , and only the  $m = 0$  terms appear in the sum of eq. (4). Consequently, the  $z$ -force  $F_z$ , which is exerted on a sphere at the origin, is given by the following expression ( $b_l \equiv b_{\mathbf{R}=0lm=0}$ ):

$$\frac{8\pi a s}{\varepsilon_h} F_z = \sum_l \left( 2l + 3 + \frac{l+1}{s} \right) \alpha_l (b_l^* b_{l+1} + b_l b_{l+1}^*), \quad (8)$$

$$\alpha_l \equiv \sqrt{\frac{l(l+1)}{(2l+1)(2l+3)}}.$$

This result is valid whatever the values of  $\varepsilon_i, \varepsilon_h$ , and can be used even if the different spheres are very close to each other, *i.e.*, when the force arises not only from induced dipole moments.

In the case where the spheres are metallic,  $\varepsilon_i \rightarrow \infty$ . We then note that  $s \rightarrow 0$  and  $b_l \propto s \rightarrow 0$ . This combines with the infinite pre-factors in eq. (8) to yield

$$4\pi a F_z = \varepsilon_h \sum_l (l+1) \alpha_l Q_l Q_{l+1}, \quad Q_l \equiv -\lim_{s \rightarrow 0} \frac{b_l}{s} = E_0 \sum_{n, \mathbf{R}} \sqrt{V_{\mathbf{R}}} \frac{U_{\mathbf{R}10}^{(n)} U_{\mathbf{0}10}^{(n)}}{s_n} = \text{real}. \quad (9)$$

The approach described above has been applied to calculate the force between two unequal metallic spheres, of radii  $a_1, a_2$ , aligned along  $z$  and subject to an external uniform field  $\mathbf{E}_0$  of magnitude 1000 V/cm in the same direction —see inset of fig. 2. Assuming the smaller sphere to have  $a_1 = 1000$  nm and the two spheres to be separated by a distance  $\delta$ , the attractive force  $F$  acting between them is plotted in fig. 1, as a function of the ratio of sphere radii  $a_2/a_1$ , for various values of  $\delta$  between  $10 a_1$  and  $0.001 a_1$ . For comparison, we also plot this force using the “dipole approximation (DA)”: Each sphere is assumed to have an electric dipole moment induced by the uniform external field, as though the other sphere were absent, and the resulting dipole-dipole force is then calculated and also plotted in fig. 1. As  $a_2/a_1$  increases, this force first increases, then reaches a maximum, and finally decreases. In the dipole approximation, this force is simply proportional to  $a_2^3/(a_1 + a_2 + \delta)^4$ , therefore the maximum occurs when  $a_2 = 3(a_1 + \delta)$  and the force tends to 0 as  $1/a_2$  when  $a_2 \gg a_1 + \delta$ . Evidently, the exact results are quite different from those obtained using DA: The magnitude of the exact force is always greater, it maximizes at a different value of the ratio  $a_2/a_1$ , and it does not tend to 0 when  $a_2$  becomes very large. The latter property is easily understood by noting that in the limit  $a_2/a_1 \rightarrow \infty$ , the larger sphere becomes a metallic half-space. Consequently, the local electric field outside the metallic constituent is the same as though an image sphere were present in that half-space. The force then has the same value as when  $a_2/a_1 = 1$  and  $\delta$  is replaced by  $2\delta$ . In fig. 2 we plot the value of the ratio of radii at maximum force  $(a_2/a_1)_{\text{max}}$  as a function of the relative separation  $\delta/a_1$  for  $\varepsilon_i/\varepsilon_h = 20$  (dielectric spheres) and  $\varepsilon_i/\varepsilon_h = \infty$  (metallic spheres), as well as the DA value, which is the same for both types of spheres. Evidently, the exact results are quite different from what the DA would lead us to expect.

We also applied the above approach to a sequence of three, successively smaller spheres and with smaller separations, also aligned along the direction  $z$  of the applied external uniform

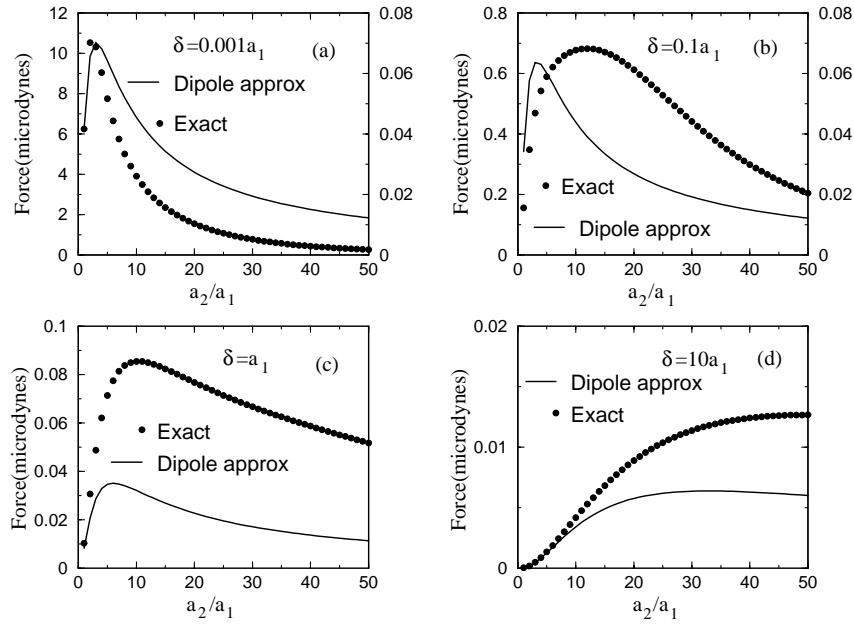


Fig. 1 – Attractive force between two metallic nanospheres, plotted *vs.* the ratio of radii  $a_2/a_1$ , for different values of the inter-sphere gap  $\delta$ , when an external uniform electric field  $\mathbf{E}_0$  of magnitude 1000 V/cm is applied along the line connecting the sphere centers (see inset of fig. 2). The radius of sphere No. 1 is fixed at  $a_1 = 1 \mu\text{m}$ . In (a) and (b), the force scales differ for the two curves: The scale on the left is for the exact results, the one on the right is for the DA results.

field. This configuration has become a subject of some interest due to the recent discovery that it can serve as a nano-lens for optical ac electric fields, if all the sphere sizes and separations are much smaller than the wavelength: When such a field is applied at a frequency which is near a highly localized quasi-static resonance of that configuration, the field can be

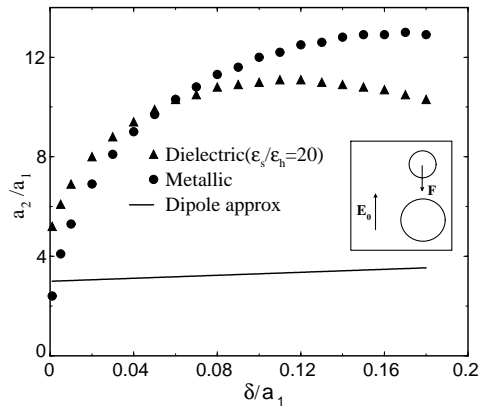


Fig. 2 – The ratio of radii at maximum force  $(a_2/a_1)_{\text{max}}$  *vs.* the relative separation between the surfaces of the two spheres  $\delta/a_1$ . The direction of the external field  $\mathbf{E}_0$  is indicated in the inset, and is the same as in the case of fig. 1. The magnitudes of  $\mathbf{E}_0$  and  $a_1$  are also as in fig. 1.

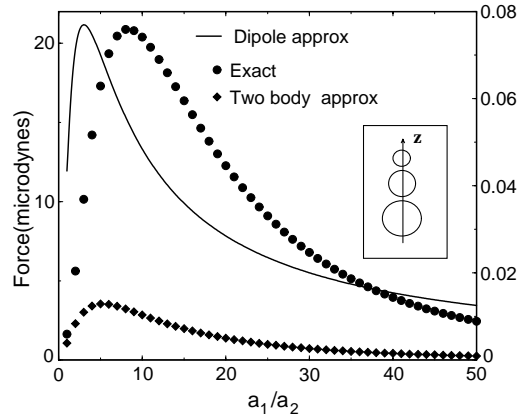


Fig. 3 – Downward force exerted on smallest metal sphere in a three-sphere nano-lens, plotted *vs.* the common radii ratio  $a_2/a_1 = a_3/a_2$ . The external electric field  $\mathbf{E}_0$  lies along the line through the three-sphere centers, its magnitude is 1000 V/cm, the radius of the smallest sphere is  $a_1 = 1 \mu\text{m}$ , and the inter-sphere gaps are  $\delta_{12} = 0.01a_1$ ,  $\delta_{23} = 0.01a_2$ . The force scale for the DA results only is on the right, while for the other two curves it is on the left.

tremendously enhanced within a region of space that is much smaller than the wavelength [14]. The force acting on the smallest sphere at one end of the sphere sequence has been calculated, and is plotted in fig. 3.

In this case, too, the dipole approximation is very bad. Moreover, even if we use the previous exact calculation of the two-body force between a pair of spheres and try to approximate the force on the smallest sphere as a sum of the two two-body forces exerted by the other spheres, we get a force that is too small by a large factor. The results of this latter calculation are also plotted in fig. 3.

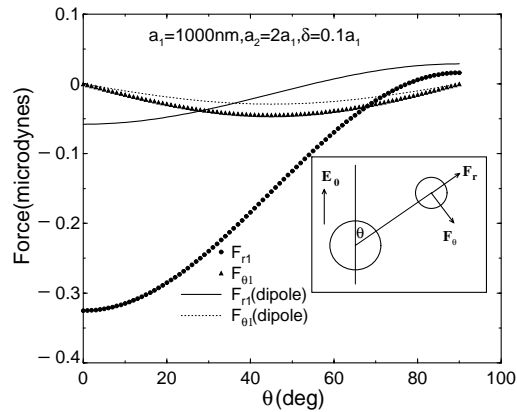


Fig. 4 – Force components  $F_{r1}$ ,  $F_{\theta1}$  exerted on sphere No. 1 (the one on the upper right in the inset) when two spheres are placed in a uniform external field  $\mathbf{E}_0$ , directed at an angle  $\theta$  with respect to the line through the sphere centers. The field magnitude is 1000 V/cm, and the radius of the smaller sphere is  $a_1 = 1 \mu\text{m}$ . The DA results for this configuration are also plotted for comparison.

In order to demonstrate the efficacy and usefulness of the method we have developed, we also considered the case of two metallic spheres in an applied uniform field  $\mathbf{E}_0$  which does not lie along the line through the sphere centers. In that case, the force acting on each sphere will have a radial component  $F_r$ , which points along the separation vector between the two sphere centers, as well as a tangential component  $F_\theta$  which is perpendicular to that line and lies in the plane defined by it and by  $\mathbf{E}_0$ . Those two force components were calculated and are plotted in fig. 4 as a function of the angle  $\theta$  between that line and  $\mathbf{E}_0$ . Also plotted are the values obtained for those force components using DA.

The approach outlined in this article can be applied to arbitrary collections of spherical inclusions embedded in a dielectric host. It should be useful for calculations of dynamics in electrorheological fluids. A full development of the method and the resulting expressions for the various force components will be published elsewhere.

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