Enhanced nonconservative forces between polarizable nanoparticles in a time-dependent electric field

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We find the time-averaged force between two polarizable particles in a uniform oscillating electric field. The force is in general noncentral, and if the dielectric function is dissipative, nonconservative. When dielectric surface modes are excited, the magnitude of the force is enhanced and its direction changes in such a way that the lines of force can spiral toward a fixed point, where the force is zero. © 2004 American Institute of Physics. [DOI: 10.1063/1.1807022]

Electrical forces on uncharged particles have been studied extensively.\textsuperscript{1} The particles can be as small as atoms or molecules, or as complicated as folded proteins or living cells. The medium can be a gas, an insulating liquid, or a complicated mixture of substances such as electrolytes and dyes. Even if they are initially unpolarized, the particles can acquire a dipole moment by their mutual interaction, or by induction from an external field. If such field is nonuniform, an isolated particle will experience a force, an effect known as dielectrophoresis.\textsuperscript{2} If the external field is uniform, the nonuniform field acting on a given particle can arise from dipoles induced on nearby particles.\textsuperscript{3} This causes forces between the particles which tend to align them into chains.\textsuperscript{4,5}

Also, the forces between nearby particles arising from the induced multipolcs can be large enough\textsuperscript{6} to explain experiments which modify the geometry of clusters of particles\textsuperscript{6,7} or increase the speed of coagulation of colloids.\textsuperscript{8}

In this letter we show that for any system of uncharged particles in a time-dependent external electric field, such as under laser illumination, the time-averaged forces between particles are noncentral and nonconservative, exhibiting a rather bizarre behavior. We assume that the particles are composed of a material with a complex dielectric function \( \varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \), and that the external field has a frequency that can excite surface modes.\textsuperscript{9} These modes are associated with peaks in the optical absorption and scattering cross sections, they appear at frequencies such that \( \varepsilon'(\omega) < 0 \), and they depend on the shapes and relative positions of the particles.\textsuperscript{3} In metals, the surface modes are often called “surface plasmons” and they occur at frequencies below the plasma frequency. For polarizable insulators with a complex dielectric function, they are called “surface phonons” and occur between the transverse optical and longitudinal optical frequencies. If a surface mode frequency passes through the fixed frequency of the external field as the particles are moved, the amplitude of the mode goes through a maximum, causing a resonant enhancement of the forces. Moreover, the mode will undergo a 180\textdegree phase change, causing the directions of the forces to change abruptly. This leads to the bizarre behavior of the lines of force.

To illustrate these ideas, we shall examine a simple system for which an analytic solution exists: two spheres of radius \( a \) in vacuum in a regime where the dipole approximation is appropriate. The center of sphere 1 is at the origin of a spherical coordinate system, and the center of sphere 2 is located at the point \((r, \theta, \phi)\). We use a dimensionless distance variable \( v = r/2a \); if the spheres touch, \( v = 1 \). There is a uniform external field \( E_0(t) = Re(E_0 e^{-i\omega t}) \) in the \( z \) direction. We are assuming the quasistatic limit: the sphere size and distance between spheres is much smaller than \( c/\omega \). The force components \( F_r \) and \( F_\theta \) are independent of \( \phi \) and the force \( F_\phi = 0 \), so we can take \( \phi = 0 \). Each sphere has a dipolar polarization \( \alpha = a^3 \varepsilon'(\omega)/[\varepsilon(\omega) + 2] \). It is useful to express this quantity as a function of the complex spectral variable \( u = u' + iu'' = 1/[1 - \varepsilon(\omega)] \). One finds \( \alpha = 1/2a^3/[1 - u] \), so the resonance condition for the dipole surface mode of an isolated sphere is \( u' = 1/2 \).

In our system with two spheres, the external field \( E_0 \) can excite two dipolar surface modes. The component of the field along the line joining the sphere centers, \( E_0 \cos \theta \), excites an “attractive mode,” with two equal dipoles \( p_\parallel \) oriented parallel to this line, and the component of the field perpendicular to this line, \( E_0 \sin \theta \), excites a “repulsive mode,” with two equal dipoles \( p_\perp \) oriented in this perpendicular direction. For the attractive mode, the field acting on each sphere is the sum of the external field and the field from the dipole on the other sphere, giving \( p_\parallel = \alpha(E_0 \cos \theta + 2p_\parallel/r^2) \). Solving for the unknown dipole moment, we find \( p_\parallel = \alpha(E_0 \cos \theta + 2p_\parallel/r^2) \). For the repulsive mode, the external field acting on a given sphere and the field produced by the dipole on the other sphere are in opposite directions, and one gets \( p_\perp = \alpha(E_0 \sin \theta - p_\perp/r^2) \). We find \( p_\perp = \alpha(E_0 \sin \theta \), where \( \alpha = 1/2a^3/(n_R - u) \), with \( n_R = 1/(1 + 1/8a^2) \).

The real part of the spectral variable, \( u' \), normally increases from 0 to 1 as \( \omega \) increases in the region where \( \varepsilon'(\omega) < 0 \) for materials such as a metallic conductor or an insulator with an isolated resonance, i.e., a narrow peak in \( \varepsilon''(\omega) \). Therefore, we will refer to \( u' \) as the “applied frequency,” and to \( n_R \) and \( n_A \) as the “frequencies” of the attractive and repulsive surface modes, respectively.\textsuperscript{10} We shall refer to \( u'' \) as the “damping,” since \( u'' \neq 0 \) for a dissipative...
material \((\epsilon'' \neq 0)\). In Fig. 1, \(n_A\) and \(n_R\) are plotted as functions of \(\sigma\). This figure shows that an intersection with the attractive mode occurs if the applied frequency is in the range 0.25 < \(u''\) < 0.333, i.e., there is a value of \(\sigma\) such that a resonance condition \(u'' = n_A\) is satisfied. We shall show that this ‘mode intersection’ is responsible for the spiraling of the force lines into a fixed point where the force \(u' = 0.32\).

If we know the components \(p_i (r, t)\) and \(p_{\perp} (r, t)\) of the dipole moments, we can find the forces on the spheres from Coulomb’s law. The force on sphere 2 is

\[
F_i (r, t) = (3/r^3)(p_{\perp}(r, t))^2 - 2p_i (r, t) t^2,
\]

\[
F_{\perp} (r, t) = - (6/r^3)p_i (r, t)p_{\perp}(r, t),
\]

and there is an equal and opposite force on sphere 1. Note that this force is noncentral. Time-averaged values are found using \(p_{\mu}(r, t)p_{\nu}(r, t) = \frac{1}{2} \text{Re} [p_{\mu}^* p_{\nu}]\), where \(p_{\mu}\) and \(p_{\nu}\) represent the complex amplitudes \(p_i\) or \(p_{\perp}\). The final result for the time-averaged force is

\[
F_i (r) = \frac{\alpha^2 E_0^2}{96\sigma^3} \left[ \sin^2 \theta \frac{n_R - u^2}{n_A - u^2} - 2 \cos^2 \theta \right],
\]

\[
F_{\perp} (r) = - \frac{\alpha^2 E_0^2}{96\sigma^3} \text{Re} \left[ \frac{2 \cos \theta \sin \theta}{n_A - u(n_R - u)^*} \right],
\]

where \(n_A\) and \(n_R\) depend on \(\sigma\). As defined above, \(\theta\) is the angle between the position vector \(r\) and the \(z\) axis.

Figure 2 shows a few lines of force in the \(xz\) plane, calculated using Eqs. (3) and (4) with applied frequency \(u' = 0.32\) and damping \(u'' = 0.01\). The force has reflection symmetry about the horizontal plane (\(\theta = 90^\circ\)), so the lines of force are shown only for \(\theta \approx 90^\circ\).

The attractive force enhancement and sign changes of \(F^i\) and \(F_{\perp}\), which cause the force lines to spiral into the fixed point as shown in Fig. 1, is at \(\sigma = 1.842\). The denominator \(|n_A - u|^2\) in the second term of Eq. (3) becomes small at this intersection distance, leading to the resonant enhancement of the attractive force, provided that \(\cos \theta\) is not too small. As \(\theta\) increases toward \(90^\circ\) and \(\cos \theta\) decreases, the first term in Eq. (3) will become larger than the second term, so the radial component of the force must change from attractive to repulsive at some angle \(\theta < 90^\circ\) for any distance \(\sigma\).
change the definition of the spectral variable to \( u = \varepsilon_m(\omega)/[\varepsilon_m(\omega) - \varepsilon(\omega)] \); (2) multiply the right-hand sides of the two equations by \( \varepsilon_m'(\omega) \).17 If the medium has isolated absorption peaks, there could be additional resonant enhancement and changes in direction of the force arising from the frequency dependence of \( \varepsilon_m'(\omega) \).

For simplicity we have worked within the dipole approximation. From accurate calculations for systems of spheres,18 it has been found that this approximation is valid only if the sphere separation \( \sigma \geq 1.5 \). At smaller separations, higher multipoles must be used to calculate the forces accurately, and as the spheres approach touching, infinitely many multipoles are needed. Because there are many mode intersections for certain ranges of \( u' \), the number of fixed points could then be very large. However, one expects at most a small number of fixed points to be resolved due to the effect of damping.

There is another effect which we have not yet mentioned: if the material is dissipative, both spheres experience a clockwise torque when sphere 2 is in the region shown in Fig. 2. The torque becomes large at a mode intersection; a clockwise torque when sphere 2 is in the region shown in Fig. 2. The torque becomes large at a mode intersection; however, it does not experience changes in sign as does the force, so even when the spheres are at the fixed point, where the force is zero, there will be a torque. This torque, and the rotational motion it causes, has been described previously.19,20

In summary, we have shown that the time-averaged forces between a pair of polarizable spheres in a uniform time-dependent electric field are noncentral, nonconservative if there is dissipation, and enhanced if surface modes are excited. It can be proved that these conclusions are also true for a system with any number of spheres of different radii. We expect them to hold much more generally, e.g., if the particles have nonspherical shapes, if the model of a uniform dielectric function is not applicable, if the various particles are composed of different materials, or if the quasistatic limit breaks down. A similar theory can be applied to a system of paramagnetic particles in a time-dependent external magnetic field, and one will find identical results for the behavior of the forces between the particles. In testing the ideas in this letter experimentally, it must be remembered that we have neglected van der Waals and gravitational forces on the particles, and have assumed they are uncharged. If the external electric field is supplied by light, there will also be forces on the particles due to the intensity gradient and Rayleigh scattering.

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9C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).
10The true surface mode frequencies for two free-electron metallic spheres with plasma frequency \( \omega_p \) and dielectric function \( \varepsilon(\omega) = 1 - \omega_p^2/\omega^2 \) are \( \omega_{s1} = \omega_p \sqrt{1/\sigma} \) and \( \omega_{s2} = \omega_p \sqrt{1/\sigma} \).
11Equations (1) and (2) have been given in a slightly different form by R. Tao and Q. Jiang, in Ref. 4, p. 325.
12If \( u' = 0 \), \( F_\psi \) is undefined when \( v_\psi = u' = 0 \), and as \( \sigma \) decreases \( F_\psi \) jumps discontinuously from \( -\infty \) to \( +\infty \) at \( \sigma = \sigma_c \). \( F_\psi \) passes through zero as it changes sign only if \( u' \neq 0 \).
14S. Lin, S. Fraden, and Y. Hu, in Ref. 4, p. 359.
17See Ref. 1, Section 2.5.