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# Classical Theory of Optical Nonlinearity in Conducting Nanoparticles

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Panasyuk, G. Y., Schotland, J. C., & Markel, V. A. (2008). Classical Theory of Optical Nonlinearity in Conducting Nanoparticles. Retrieved from http://repository.upenn.edu/be_papers/107

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Publisher URL: http://dx.doi.org/10.1103/PhysRevLett.100.047402

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**Abstract**
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**Keywords**
optical properties of nanocrystals and nanoparticles, relaxation oscillations and long pulse operation of lasers, dynamics of nonlinear optical systems, high-field transport and nonlinear effects (semiconductors/insulators)

**Comments**
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Publisher URL: http://dx.doi.org/10.1103/PhysRevLett.100.047402

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# Classical Theory of Optical Nonlinearity in Conducting Nanoparticles

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(Received 10 August 2007; published 29 January 2008)

We develop a classical theory of electron confinement in conducting nanoparticles. The theory is used to compute the nonlinear optical response of the nanoparticle to a harmonic external field.

DOI: 10.1103/PhysRevLett.100.047402 PACS numbers: 78.67.Bf, 42.60.Rn, 42.65.Sf, 72.20.Ht

Fundamental and applied research in the area of plasmonic nanodevices and of engineered materials constructed from plasmonic nanoparticles is at the center of modern optics [1,2]. Most theoretical approaches to such systems are based on the classical electrodynamics of continuous media. However, in the case of nanoparticles whose linear dimensions are not dramatically larger than the atomic scale (a factor of $\sim 10$ is typical), finite-size and quantum corrections are of importance [3]. Previously, the above two terms have been used interchangeably, and it is accepted that the small-size effects are quantum mechanical in origin. Thus, they can be understood by considering discrete electron states in a nanoparticle [4,5] or reduction of interband screening and electron spillover near the nanoparticle surface [6,7]. In this Letter, we demonstrate that there is an additional, purely classical mechanism that leads to finite-size effects and, in particular, to nonlinearity of the electromagnetic response of conducting nanoparticles. We refer to this mechanism as the classical confinement effect.

In this work, we develop a theory of classical confinement of electrons in conducting subwavelength-sized nanoparticles and derive nonlinear polarizabilities in 1D (slab) and 3D (sphere) geometries. Our theory is nonperturbative and fully accounts for electron-electron interactions within the accuracy of the quasistatic approximation. The predicted effects differ from other optical nonlinearities, most importantly, by the unusual dependence of the nonlinear response on the intensity of the incident laser beam.

The size-dependent nonlinear susceptibilities of a conducting nanoparticle were theoretically calculated in Refs. [4,5] from first principles. A conducting nanosphere was modeled as a degenerate electron gas placed in an infinitely high confining potential and subjected to a time-harmonic external electric field. In this model, the optical nonlinearity is a consequence of the saturation of optical transitions between discrete electronic states; however, the confinement effect that we discuss in this Letter is not taken into account. Thus, for example, in Ref. [5], a Hamiltonian was used with the interaction term $V = e\mathbf{r} \cdot \mathbf{E}$ where $\mathbf{E} = f\mathbf{E}_{\text{ext}}$, $\mathbf{E}_{\text{ext}}$ being the external field and $f = [1 + (\epsilon - 1)/3]^{-1}$ the Lorentz factor. In other words, it was assumed that the electrons move in an electric field that is obtained from the solution to the Laplace equation, which does not account for finite-size effects. We further note that in the quantum theory of Ref. [5], there are two different contributions to polarization of the nanosphere: one due to off-resonant transitions between electron states near the Fermi surface and the other due to resonant transitions between states separated by the energy gap $\hbar\omega$. In our model, only the first (Drudean) contribution is taken into account. As a result, the relaxation constant $\gamma$ introduced below is size independent. We can, however, take into account its size dependence phenomenologically by writing $\gamma = \gamma_\infty + v_F/a$, where $\gamma_\infty$ is the respective value in a bulk conductor and $v_F$ is the Fermi velocity.

We begin by noting that the classical electrodynamic theory of conductors is based on the implicit assumption that the volume density of free charge is infinite. More specifically, the atomic lattice is assumed to be rigid and to carry a uniform positive volume charge while free electrons form a negatively charged compressible fluid. If we apply an external field $E_{\text{ext}}$, the two volume charges shift with respect to each other by a distance $\delta$, which results in the formation of a surface charge with density $\sigma$. From the linearity of the Laplace equation, it follows immediately that $\sigma \propto \delta \propto E_{\text{ext}}$. However, the volume charge densities are assumed to be so large that, irrespective of the magnitude of the external field, the shift $\delta$ is much smaller than any other physical scale in the problem. This assumption is exceedingly accurate for macroscopic conductors. But in nanoparticles, a nonzero value of $\delta$ can result in experimentally observable nonlinearity.

We now proceed with detailed calculations. As a first step, consider the one-dimensional problem schematically illustrated in Fig. 1(a). Here an external field $E_{\text{ext}} = -E_0$ is directed perpendicularly to a slab of thickness $L$. If $E_0 > 0$, the free charge is distributed inside the slab as follows. The surface that is opposite the field direction (as shown in the figure) acquires a negative surface charge $\sigma_2 = -E_0/4\pi$. Near the other surface, a positively charged layer of depth $h = E_0/4\pi\rho$ is formed, where $\rho = Ze/\ell^3$ is the background positive volume charge density. Here $Z$ is the number of free electrons per atom, $e$ is the electron charge, and $\ell$ is the lattice constant; we have assumed a cubic lattice and neglected surface roughness. We thus see that the slab is separated into two regions. The first region is characterized by zero conductivity due to the absence of

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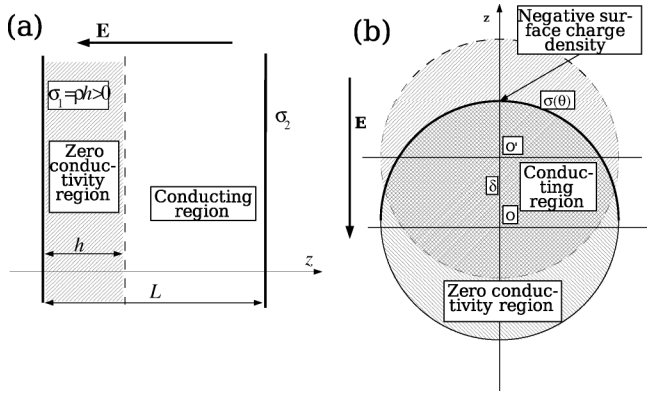


FIG. 1. Illustrating the geometry of the 1D (a) and 3D (b) problems.

free carriers [this region is dashed in Fig. 1(a)] while the second region is conducting. In static equilibrium, the local field in the second region must be zero, while there is no such requirement for the first region. We note that the field inside the conducting region, which is produced by the positively charged layer, is $2\pi\sigma_1$ where $\sigma_1 = E_0/4\pi$, the same as would be produced by a surface charge of density $\sigma_1$. Thus, the depolarizing field inside the conducting layer is $E_{\rm dep} = 2\pi(\sigma_1 - \sigma_2) = E_0$ and the total local field $E_{\rm loc} = E_{\rm ext} + E_{\rm dep}$ is zero.

Next, consider a time-varying external field $\tilde{E}_{\rm ext}(t) = E_0 \exp(-i\omega t)$. Here and thereafter, we denote the complex representation of physical observables by a tilde; the corresponding real quantities are obtained by adding a complex conjugate, i.e., $E = \tilde{E} + \tilde{E}^*$. The positively charged layer can now appear on either side of the slab. It is convenient to introduce the following notation: let the total charge per unit area that accumulates near the left face of the slab be $\sigma_1$ and the similar quantity near the right face be $\sigma_2$. Here we do not distinguish between a true surface charge and a surface layer of finite depth. It follows from charge conservation that $\sigma_1 = -\sigma_2$. We then can write $\sigma_1 = -\sigma$, $\sigma_2 = +\sigma$, where $\sigma$ can be either positive or negative, depending on the phase of the oscillations. The depolarizing field in the conducting region is given at any time by $E_{\rm dep} = -4\pi\sigma$ and the total local field by $E_{\rm loc} = E_{\rm ext} + E_{\rm dep}$. Then the equations of motion for a negative test charge inside the conducting region can be written as

$$m(\dot{v} + \gamma v) = -e[E_{\rm ext}(t) - 4\pi\sigma], \qquad \dot{\sigma} = -\rho v. \quad (1)$$

Here $v$, $m$, and $e$ are the electron velocity, mass, and charge, respectively, and $\gamma$ is a phenomenological friction term; the first equation in (1) is Newton's second law while the second is the continuity equation. The oscillatory solution to the above system of ordinary differential equations is

$$4\pi\tilde{\sigma}(t) = \omega_p^2 E_0 e^{-i\omega t}[\omega_p^2 - \omega^2 - i\gamma\omega]^{-1}, \quad (2)$$

where $\omega_p = \sqrt{4\pi e\rho/m}$ is the plasma frequency. We can further compute the local field $E_{\rm loc}$ and the current $j = -\rho v$ inside the conducting region and verify that the ratio $\tilde{j}(t)/\tilde{E}_{\rm loc}(t)$ yields the classical Drude conductivity $i\omega_p^2/4\pi(\omega + i\gamma)$.

So far, the results appear to be conventional. Finite-size effects and the nonlinearity of the optical response become apparent when we compute the dipole moment per unit area of the slab, $\mathcal{P} = \Delta d/\Delta S$. A straightforward calculation yields $\mathcal{P}(t) = \sigma(t)[L - h/2]$. Thus, the effective width of the slab is reduced by $h/2$ where $h = |\sigma|/\rho$ (note that $h$ is related to the absolute value of the real-valued quantity $\sigma$). We now find that $\mathcal{P}(t) = \sigma(t) \times [L - (1/2\rho)|\sigma(t)|]$. We further note that the field amplitude $E_0$ can always be chosen to be real so that $\sigma(t) = (2\pi)^{-1} E_0 \Lambda(\omega)\cos(\tau)$, where $\tau = \omega t - \varphi$, $\tan\varphi = \gamma\omega/(\omega_p^2 - \omega^2)$, the resonant factor $\Lambda(\omega)$ is given by

$$\Lambda(\omega) = \omega_p^2/\sqrt{(\omega_{\rm res}^2 - \omega^2)^2 + (\gamma\omega)^2}, \quad (3)$$

and the resonance frequency (specific to the planar geometry) is $\omega_{\rm res} = \omega_p$. We then write the final result as

$$\mathcal{P}(t) = (2\pi)^{-1} L\Lambda(\omega) E_0[\cos\tau + \beta\cos\tau|\cos(\tau)|], \quad (4)$$

where $\beta = -(2\pi)^{-1}\Lambda(\omega)|E_0|/2\rho L = -(2\pi)^{-1}\Lambda(\omega) \times (\ell/2L)|E_0/E_{\rm at}|$ and we have introduced the atomic field $E_{\rm at} = Ze/\ell^2$. Thus it can be seen that the theory has two small parameters: $E_0/E_{\rm at}$ and $\ell/L$. The first parameter is typical in nonlinear optics. The second small parameter, $\ell/L$, is negligibly small for macroscopic conductors. However, for $L \sim 5$ nm and $\ell \sim 0.5$ nm (silver), the ratio is $\sim 1/10$.

Note that (4) is not an expansion but is exact as long as $h < L$ or, equivalently, $\max(|\sigma|) < \rho L$. The important feature of the obtained solution is that $\mathcal{P}(E_0)$ is not an analytic function and cannot be expanded into a Taylor series. This mathematical property is closely related to the existence of a finite limit $\lim_{E_0\to\infty}\mathcal{P}(E_0)$ (in the saturation model of Refs. [4,5] this limit is zero).

We now consider the problem of a three-dimensional conducting sphere. It turns out that accounting for classical confinement in this case leads to a formidable mathematical problem. We will use, however, certain physical insights that will allow us to obtain a nonperturbative analytical theory. Consider a conducting sphere of radius $a$, a constant background positive volume charge $\rho$, and a free charge whose integral over the sphere volume is $-4\pi a^3\rho/3$; an infinitely high spherical potential barrier that prevents ionization is assumed. We seek to find the dipole moment of the sphere in an external field $\tilde{\mathbf{E}}_{\rm ext} = \hat{\mathbf{z}} E_0 \exp(-i\omega t)$, where $\hat{\mathbf{z}}$ is a unit vector pointing in the direction of the $z$ axis. As before, we recognize that the sphere is separated at all times into two regions: one region has no free carriers and is nonconducting while the other region has a constant nonzero conductivity; this conducting region is doubly dashed in Fig. 1(b). The existence of a well-defined boundary between the conducting and nonconducting regions is a consequence of the quasistatic

limit, as follows from the Maxwell equation $\nabla \cdot \mathbf{P} = 0$ ($\mathbf{P}$ is the macroscopic polarization), which is valid everywhere inside the particle except for its boundary and the surface that separates the conducting and nonconducting regions, at which surfaces the medium properties change abruptly.

The first physical observation that we make is that in the quasistatic problem with a time-harmonic external field, the motion of charges is such that, at any time $t$, both the volume and the surface charge densities correspond to a static equilibrium obtained for an external field $A(\omega)\mathbf{E}_{\text{ext}}(t')$, which is taken at a different time $t'$ and multiplied by a frequency-dependent real-valued factor $A(\omega)$. Thus, the system goes through states of static equilibrium that are phase shifted with respect to the external field. Mathematically, this statement follows from the linearity of the equations of motion. In static equilibrium, the electric field in the conducting region is zero. In the dynamic problem, the latter is nonzero but proportional to the difference $\mathbf{E}_{\text{ext}}(t) - \mathbf{E}_{\text{ext}}(t')$. We assume here that $\mathbf{E}_{\text{ext}}$ is spatially homogeneous over the volume of the sphere. The only motion of the free charge inside the conducting region that is consistent with this condition is one-dimensional motion along the $z$ axis. From this, we find that the surface that separates the conducting and nonconducting regions is a sphere. The center of this sphere is denoted by $O'$ and is shifted from the center of the original sphere by a distance $\delta$ along the $z$ axis, where $\delta$ can be both positive and negative [see illustration in Fig. 1(b)]. We thus can characterize the dynamics of the system by a single scalar parameter $\delta$.

The second observation will allow us to find the depolarizing field inside the conducting region. As we have argued above, the total electric field inside that region is spatially homogeneous and directed along the $z$ axis. The external field does satisfy this condition and so must the depolarizing field $\mathbf{E}_{\text{dep}}$. The latter is a superposition of the field produced by a positively charged meniscus and the negative surface charge $\sigma$, which we have not yet determined. We notice, however, that a field with the required properties is created by two oppositely charged menisci of the same shape, which are shown in Fig. 1(b) as single-dashed regions. Indeed, the field produced by the two menisci is the same as the field of two oppositely charged spheres shifted with respect to each other by a distance $\delta$. Inside the conducting region, this field is given by $\mathbf{E}_{\text{dep}} = 4\pi\rho\delta\hat{\mathbf{z}}/3$. With the understanding that this field is created by the positively charged meniscus and by a yet unknown negative surface charge $\sigma$ whose field in the conducting region is the same as that of the hypothetical negatively charged meniscus, we write the equation of motion as

$$m(\ddot{\delta} + \gamma\dot{\delta}) = -e[\hat{\mathbf{z}} \cdot \mathbf{E}_{\text{ext}}(t) + 4\pi\rho\delta/3]. \quad (5)$$

The oscillatory solution to (5) is

$$\tilde{\delta}(t) = -(e/m)E_0 e^{-i\omega t}[\omega_F^2 - \omega^2 - i\gamma\omega]^{-1}, \quad (6)$$

where $\omega_F = \omega_p/\sqrt{3}$ is the Frohlich frequency. In the conventional approach, the dipole moment of the sphere is computed as $\tilde{d} = -4\pi\rho a^3\tilde{\delta}/3$. Evaluation of this expression leads to the linear polarizability $\alpha = a^3(\epsilon - 1)/(\epsilon + 2)$ with $\epsilon = 1 - \omega_p^2/\omega(\omega + i\gamma)$. We, however, intend to take into account the presence of the meniscus and the fact that the surface charge density can deviate from the usual $\propto \cos\theta$ dependence. To this end, we write $d_z = \hat{\mathbf{z}} \cdot \mathbf{d} = \rho \int_V z d^3r + \int_S z\sigma d^2r$. Here the first integral is over the volume of the positively charged meniscus while the second term is the contribution of the negative surface charge. After tedious but straightforward integration, we obtain

$$\frac{d_z}{2\pi} = -\frac{\rho\delta}{3}\left[a^3 - |\delta|\left(\frac{3a^2}{4} - \frac{\delta^2}{16}\right)\right] + a^3\sigma_1, \quad (7)$$

where $\sigma_1 = \int \sigma(\cos\theta)\cos\theta d\cos\theta$. We thus see that knowledge of the first moment of the surface charge density suffices for the purpose of computing the dipole moment. We find $\sigma_1$ by considering the depolarizing potential in the vicinity of the sphere origin, $O$. On one hand, we know that the potential is given by $\phi = -E_{\text{dep}}z$ with $E_{\text{dep}} = 4\pi\rho\delta/3$. On the other hand, we can write the same potential as an integral over the meniscus and the surface of the sphere and expand the resultant formula into scalar spherical harmonics $r^l Y_{lm}(\hat{\mathbf{r}} \cdot \hat{\mathbf{z}})$. A straightforward calculation of the term $l = 1$, $m = 0$ yields $\phi_{10} = 2\pi\{\sigma_1 - (\rho\delta/3)[1 + (3|\delta|/8a)]\}z$. From the equality $\phi_{\text{dep}} = \phi_{10}$, it follows that $\sigma_1 = -(\rho\delta/3) \times [1 - (3|\delta|/8a)]$. We then substitute the above result into (7) to find

$$d_z = -\frac{4\pi\rho\delta a^3}{3}\left[1 - \frac{9}{16}\frac{|\delta|}{a} + \frac{1}{32}\frac{\delta^2|\delta|}{a^3}\right], \quad (8)$$

where $\delta = \tilde{\delta} + \tilde{\delta}^*$ and $\tilde{\delta}$ is given by (6). We emphasize that the above formula is not an expansion: it is exact as long as $|\delta| < a$, the latter condition having been implicitly used for computing $\sigma_1$.

The term $\propto \delta^3|\delta|$ in (8) can be neglected as small. The term $\propto \delta|\delta|$ describes the generation of odd-order frequency harmonics. Indeed, let $E_0$ be purely real, so that $\delta|\delta| \propto \cos(\tau)|\cos(\tau)|$, where $\tau = \omega t - \varphi$, and consider the following Fourier series:

$$\cos(\tau)|\cos(\tau)| = \sum_{k=2n+1, n\geq 0} \frac{8(-1)^n \cos(k\tau)}{\pi k(4 - k^2)}. \quad (9)$$

A similar series for $\cos^3(\tau)|\cos(\tau)|$ also contains only odd-order harmonics. Note that even though the nonlinear corrections are second order in $E_0$, there is no second-harmonic generation. Generation of the third harmonic ($n = 1$) and nonlinear refraction ($n = 0$), which are traditionally associated with the third-order nonlinear susceptibility $\chi^{(3)}$, are manifest in the model to second order in $E_0$.

Neglecting the third term in the square brackets in Eq. (8) and using (6) for $\tilde{\delta}$, we find

$$d_z = (1/3)a^3\Lambda(\omega)(2E_0)[\cos\tau + \beta\cos\tau|\cos\tau|], \quad (10)$$

where $\Lambda(\omega)$ is given by (3) with $\omega_{\rm res} = \omega_F$ and $\beta = -(3/4)^2\Lambda(\omega)|2E_0|/4\pi\rho a$. To obtain the nonlinear correction to the refractive index $n$, we retain only the $k = 1$ term in the Fourier series (9). For a transparent medium of refractive index $n_0$ doped with randomly and sparsely distributed metal nanospheres, we have

$$n^2 = n_0^2\left[1 + 3p\frac{\omega_F^2}{\omega_F^2 - \omega^2 - i\gamma\omega}\left(1 + \frac{8\beta}{3\pi}\right)\right], \quad (11)$$

where $p$ is the volume fraction of the metal and we have used the Maxwell-Garnett mixing rule. Note that although we have assumed an infinitely high potential barrier around the nanosphere so that its polarizability is formally independent of $n_0$, we can account for this dependence phenomenologically by writing $\omega_F^2 = \omega_p^2/(2n_0^2 + 1)$.

The coefficient $\beta$ can be written as $\beta = \sqrt{W/W_c}$ where $W$ is the power of the incident beam, $W_c = 4\pi(4/3)^4 \times (a/\ell)^2 W_{\rm at}/\Lambda^2(\omega)$, and $W_{\rm at} = cZ^2e^2/\ell^4$. For silver, $Z = 1$, $\ell \approx 0.5$ nm, and $W_{\rm at} \approx 1.2 \times 10^{15}$ W/cm$^2$. The nonlinearity is maximized when $\Lambda = \Lambda_{\rm res} = \sqrt{3}\omega_p/\gamma$. We take into account the size dependence of $\gamma$ by writing $\gamma = \gamma_\infty(1 + a_0/a)$. For silver, $a_0 = v_F/\gamma_\infty \approx 50$ nm and $\omega_p/\gamma_\infty \approx 500$. For $a = 10$ nm, $\Lambda_{\rm res}^2 \approx 2 \times 10^4$. Combining all the numerical factors, we find that $W_c \approx 7.6 \times 10^{13}$ W/cm$^2$. Thus, at the experimental power $W = 10$ kW/cm$^2$ (easily attainable in nanosecond laser pulses), the ratio of the magnitudes of linear and nonlinear polarizabilities is of the order of $10^{-5}$.

In the model of classical confinement, the nonlinear polarizability is proportional to $\sqrt{W/W_c}$. Correspondingly, intensity of the generated harmonics of all orders is proportional to $W/W_c$. Therefore, the predicted effect can be distinguished from other optical nonlinearities by investigating the nonlinear response as a function of $W$. We note that the experimental data of Ref. [8] for the dependence of nonlinear absorption on $W$ cannot be explained by the conventional model of the third-order nonlinearity but is in line with the theory developed above (the curve representing the nonlinear absorption as a function of $W$ deviates from a straight line and curves down resembling the square-root dependence).

Next, we discuss the dependence of the nonlinear polarizabilities on the sphere radius, $a$. Apart from a trivial overall factor, we have $\beta = -\sqrt{W/W_c} \propto \Lambda(\omega)\ell/a$. Far from resonance, $\Lambda(\omega) \approx \omega_p^2/|\omega_F^2 - \omega^2|$ and $\sqrt{W/W_c} \propto \ell/a$. At resonance, a different dependence is obtained. Indeed, for $\omega \approx \omega_F$, we have $\Lambda \approx \Lambda_{\rm res} = \sqrt{3}(\omega_p/\gamma_\infty)/(1 + a_0/a)$ and $\sqrt{W/W_c} \propto \ell/(a + a_0)$. In Ref. [9], degenerate four wave mixing was used to measure the effective nonlinear susceptibility $\chi^{(3)}$ for glasses doped with Ag and Cu nanospheres of varying sizes (see also Ref. [10] where these data were compared to the analytical model of Ref. [5]). It was reported that $\chi^{(3)}$ tends to increase with the radius. We, however, note that the quantity measured in Ref. [9] cannot be easily related to the nonlinear polarizability derived here. On the other hand, one can argue on physical grounds that any nonlinearity that is a consequence of electron confinement should vanish in the limit $a \to \infty$, as follows from our model.

To conclude, we mention some of the limitations of the classical confinement model. First, it applies only to particles that contain many atoms and, therefore, can be viewed as macroscopic. In the case of a silver nanosphere, the theory is valid for radii larger than a few nanometers. Second, our theory is quasistatic and does not take into account retardation and radiative losses. Radiative corrections to the quasistatic polarizabilities are important when wave propagation in nonlinear media is considered and must be included to ensure energy conservation, while retardation effects can become important for higher-order harmonic generation. Third, the theory does not account for electron tunneling or "spillover" beyond the particle boundaries. If the dynamics of free electrons is quantum, it is possible to consider a potential barrier of finite height that would allow such tunneling. However, if the dynamics is classical, stability of the system requires that free charge motion is restricted to the region occupied by the rigid positively charged lattice of ions. As is typical in the classical electrodynamics of continuous media, the confining potential is not electrodynamic in nature but is introduced phenomenologically to guarantee the system's stability. Finally, the theory is not kinetic and does not take into account Fermi statistics. As a result, it is independent of Fermi's energy, except for the phenomenological dependence of the relaxation constant on the particle size.

This research was supported by the NSF under Grant No. DMR 0425780 and by the AFOSR under Grant No. FA9550-07-1-0096.

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