PHYSICAL REVIEW B VOLUME 59, NUMBER 3 15 JANUARY 1999-I

Far-infrared absorption in small metal particles

A. V. Plyukhin and A. K. Sarychev
Scientific Center for Applied Problems in Electrodynamics, 127412 Moscow, Russia

A. M. Dykhne
Scientific Center TRINITI, 142092 Troitsk, Moscow region, Russia

(Received 20 July 1998; revised manuscript received 15 September 1998)

We analyze the effects of an enveloping electron cloud on the absorption by small metal particles. We present the simplified quasiclassical kinetic model that allows us to treat the problem self-consistently and to write down the explicit response functions. If the surrounding medium is vacuum or a dielectric continuum thus obtained far-infrared absorption is orders of magnitude larger than in a classical treatment for a sharp interface. It is shown, however, that the surface absorption is sensitive to the microscopic potential landscape outside the particle and in some cases may be suppressed. [S0163-1829(99)03903-X]

In 1975 Tanner, Sievers, and Buhrman observed the anomalously enhanced far-infrared (FIR) absorption in a dilute mixture of small metal particles.[1] Since then, many experiments have shown that the magnitude of the FIR absorption for various metal nanoparticles is a few orders of magnitude larger than the predictions of classical Mie theory, which relies upon the bulk metal dielectric function. It is generally accepted now that the clustering of particles may lead to enhanced absorption.[2–6] However, it remains unclear whether the clustering is the only mechanism leading to anomalous absorption. There are only few experiments, often contradicting each other, to verify the existence of anomalous absorption by nonclustered nanoparticles. Kim and Tanner studied aluminum small particles embedded in a KCl host, finding a substantial increase in FIR absorption even in samples that do not show long-range clustering in the electron microscope studies.[6] Their data show the enhancement factor 10^3 with respect to the classically calculated electric-dipole absorption, and 10^2 if eddy currents (magnetic-dipole absorption) is also taken into account. In this experiment the particles with radius of approximately 100 Å have been studied. As the size of the particle gets larger, the FIR absorption will converge to the classical value, dominated by the magnetic dipole absorption, which increases quadratically with particle radius. This has been demonstrated by Lee *et al.*[7] for well-isolated Ag particles with the mean radius 450 Å in a Teflon host. These authors found that the ratio of the measured absorption to the calculated one is only about a factor of 3. However, even in this case quantitative agreement (i.e., the explanation of the leaving factor of 3) could be achieved only if electric-dipole absorption is enhanced by the factor 10^3 and becomes comparable (for 450-Å particles) with magnetic-dipole absorption. Lee *et al.* attribute such enhancement to the effect of absorbing oxide coating. On the other hand, Devaty and Sievers found no evidence for anomalously enhanced absorption by well-dispersed silver particles in a gelatin matrix.[2] Though their data do not exclude completely the possibility of enhanced absorption, the maximum measured enhancement has not been greater than about a factor of 10. To our knowledge, no experiments have been carried out to determine whether these results are general or unique to Ag-gelatin composites.

Despite the lack of convincing demonstration by experiment, the possibility of anomalous absorption by isolated particles has been intensively discussed by theorists. A number of mechanisms intrinsic to isolated nanoparticles has been proposed. They include vibrations,[8,9] quantum size effects,[10] electron-phonon coupling,[11] and dielectric surrounding.[12] A more general model, based on a realistic treatment of the surface region of a metal particle has been discussed by Apell.[13] He has shown that allowing for a smooth transition in the electronic properties of the surface, i.e., taking into account the real electron density profile, can greatly increase the absorption. Using the induced charge-density profile calculated by Persson and Lang within the local-density functional approach for the plane surface,[14] Apell found that absorption caused by a smooth transition of the dielectric properties at the interface is about one order of magnitude larger, for the electric dipole term, than in a classical treatment for a sharp interface. Note that Persson-Lang results has been obtained under the assumption that electrons respond adiabatically to the external field and almost adjust to the instantaneous static configuration. It may be argued that this assumption is unreasonable, because the local plasma frequency in the region of electron density tail far enough from the boundary is less than the frequency of external field. In this paper we consider the response properties of a diffuse metal surface using a much simplified but self-consistent kinetic model that allows us to get the result without adiabatical response approximation. We shall show that this model may give much larger absorption than Apell's result.

We shall treat electrons as quasiclassical particles moving in the field of a uniformly and positively charged ion background and an external ac field. We are interested in the absorption within a thin surface layer where electron density falls rapidly. The thickness of this layer is assumed to be much smaller than the particle size. Therefore we can consider a plane geometry with the x axis perpendicular to the surface of the particle. Let us assume for simplicity that the external field direction coincides with the x axis and that the electron distribution is uniform in all other directions. We use the simplest kinetic model treating the velocity space of electrons as one-dimensional and assuming that the velocity at given point x can take only two value $V(x)$ and $-V(x)$ and its direction coincides with the x axis. Then the dynamics of electrons is determined by the following equations for local numbers of electrons moving in positive and negative direction along the x axis:

$$\frac{\partial N^+}{\partial t}=-\frac{\partial}{\partial x}(VN^+)+\frac{eEN}{2mV}-\frac{N^+-N^-}{2\tau}, \tag{1}$$

$$\frac{\partial N^-}{\partial t}=\frac{\partial}{\partial x}(VN^-)-\frac{eEN}{2mV}+\frac{N^+-N^-}{2\tau}. \tag{2}$$

Here N^+ and N^- are the local densities of electrons having velocity V and $-V$, respectively; $N=N^+ + N^-$ is the total electron density; E is the local electric field, which satisfies the Poisson equation

$$\frac{\partial E}{\partial x}=4\pi e(N-N_i), \tag{3}$$

where N_i is the positive ion density. The second terms in the right-hand sides of Eqs. (1) and (2) represent the time rate of change of electron distribution due to the field action $(dN^{\pm}/dt)_f$. Indeed, the local momentum density for the two-velocity model has the form $P=mV(N^+ - N^-)$ and its variation under the field action is equal to $(dP/dt)_f = mV[(dN^+/dt)_f-(dN^-/dt)_f)]=eEN$. It follows from the charge conservation law that $(dN^+/dt)_f=-(dN^-/dt)_f$; therefore $(dN^{\pm}/dt)_f=\pm eEN/(2mV)$. The last terms in the right-hand sides of Eqs. (1) and (2) describe the relaxation transitions of electrons between V and $-V$ states with the rate $1/2\tau$.

When an external ac field with frequency ω is applied we express the electron density and field appearing in Eqs. (1)–(3) in terms of an equilibrium value plus perturbation due to external field: $N^{\pm}=N_0(x)/2+N_1^{\pm}(x)\exp(-i\omega t)$, $E=E_0(x)+E_1(x)\exp(-i\omega t)$. Then we have the following equations for the equilibrium electron density N_0 and intrinsic electric field E_0:

$$\frac{d}{dx}(VN_0)=\frac{eE_0N_0}{mV}, \quad \frac{dE_0}{dx}=4\pi e(N_0-N_i). \tag{4}$$

For a bulk metal these equations have trivial solution $N_0=N_i=\text{const}$, $E_0=0$. The equations for the perturbations due to the external field are

$$-i\omega N_1^+ + \frac{d}{dx}(VN_1^+)-\frac{eE_0N_1}{2mV}-\frac{eE_1N_0}{2mV}+\frac{N_1^+-N_1^-}{2\tau}=0, \tag{5}$$

$$-i\omega N_1^- - \frac{d}{dx}(VN_1^-)+\frac{eE_0N_1}{2mV}+\frac{eE_1N_0}{2mV}-\frac{N_1^+-N_1^-}{2\tau}=0, \tag{6}$$

$$\frac{dE_1}{dx}=4\pi eN_1, \tag{7}$$

where $N_1=N_1^+ + N_1^-$. For a bulk metal all quantities in Eqs. (5)–(7) remain independent of x even in the presence of an external field. Then we obtain from these equations that the current density $j=eV(N_1^+-N_1^-)$ is given by usual Ohm's law $j=\sigma(\omega)E_1$ with Drude conductivity $\sigma(\omega)=\sigma_0/(1-i\omega\tau)$, $\sigma_0=e^2N_i\tau/m$. In the limit $\tau\to\infty$ Eqs. (5)–(7) give the plasma oscillations with the well-known quadratic dispersion law $\omega^2(k)=\omega_p^2+V^2k^2$, where $\omega_p^2=4\pi e^2N_i/m$.

We consider now the role of spatial variation of electron density near a particle edge. We assume that the spatial scale R_D of the electron density variation is much smaller than the particle size a. Then we can use the plane boundary approximation when ion background fills the half-space $x<0$, i.e., the ion background density is equal to N_i at $x<0$ and is zero otherwise. The electron density tail decays exponentially for $x>0$. To reproduce this quantum-mechanical result within our quasiclassical model we assume, rather arbitrarily, that the electron velocity varies as $V(x)=V_F[N_0(x)/N_i]^{1/2}$, where V_F has the meaning of the Fermi velocity in the bulk metal. Then Eqs. (4) gives the equilibrium density $N_0(x)/N_i=\theta(-x)\pm(1/2)\exp(\mp x/R_D)$ and intrinsic field $E_0(x)=-2\pi eR_DN_i\exp(\mp x/R_D)$, where $R_D=(3mV_F^2/8\pi e^2N_i)^{1/2}$, $\theta(x)$ is the unit step function. The upper and lower signs correspond to the regions $x>0$ and $x<0$, respectively. The intrinsic field $E_0(x)$ corresponds to the usual double-layer field at the metal boundary. The spatial scale R_D for the field and density variation coincides with the Debye length (up to some numerical factor of the order of one). It is not surprising since the Debye length is a single spatial scale in the model other than particle size a.

Let the external ac field E_{ex} is applied in the x direction (perpendicular to the surface). Then the current density for $x\to\infty$, i.e., in the region with no charge, can be written as $I=-i\omega E_{ex}/(4\pi)$. Summing Eqs. (5) and (6) and using Eq. (7) we obtain the conservation law for the full current I:

$$I=j(x)-\frac{i\omega}{4\pi}E_1(x)=-\frac{i\omega}{4\pi}E_{ex}, \tag{8}$$

where $j(x)=eV(N_1^+-N_1^-)$ is the electron drift current. Subtracting Eq. (6) from (5) and using Eq. (8) we obtain the following equation for the dimensionless electric field $f(y)=E_1(y)/E_{ex}$ as a function of dimensionless variable $y=x/R_D$:

$$f''(y)+\frac{N_i}{N_0}\left(\frac{1}{2}\frac{d}{dy}\frac{N_0}{N_i}-\frac{eE_0R}{mV_F^2}\right)f'(y) + \frac{3}{2}\left[\left(\frac{\omega^2}{\omega_p^2}+\frac{i\omega}{\tau\omega_p^2}\right)\frac{N_i}{N_0}-1\right]f(y)=\frac{3}{2}\left(\frac{\omega^2}{\omega_p^2}+\frac{i\omega}{\tau\omega_p^2}\right)\frac{N_i}{N_0}. \tag{9}$$

We consider first the case when $1/\tau\to 0$ and losses in the bulk metal are negligible. Then using the found above expressions for the equilibrium intrinsic field $E_0(y)$ and electron density $N_0(y)$ we can rewrite Eq. (9) as

$$f''(y)+f'(y)+\left(3\exp(y)\frac{\omega^2}{\omega_p^2}-\frac{3}{2}\right)f(y)=3\exp(y)\frac{\omega^2}{\omega_p^2} \tag{10}$$

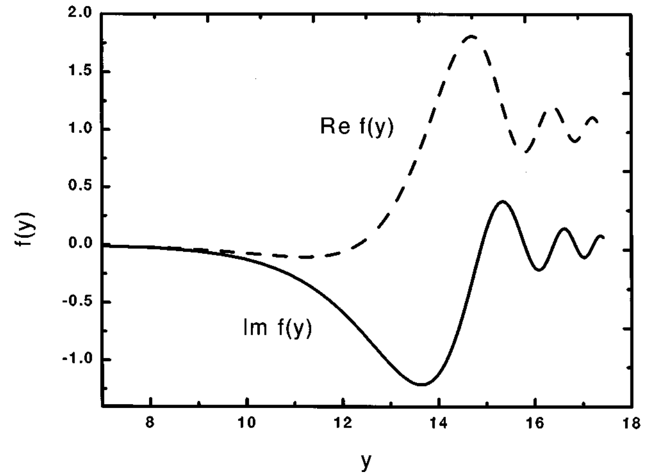

FIG. 1. Imaginary (solid line) and real (dashed line) parts of the dimensionless electric field $f=E_1/E_{ex}$ in the electron density tail region $x>0$ plotted as a function of $y=x/R_D$ for the case $\omega/\omega_p=10^{-3}$.

for $y>0$ and

$$f''(y)+\frac{\exp(y)}{2-\exp(y)}f'(y)+\left(\frac{3}{2-\exp(y)}\frac{\omega^2}{\omega_p^2}-\frac{3}{2}\right)f(y)$$

$$=\frac{3}{2-\exp(y)}\frac{\omega^2}{\omega_p^2} \tag{11}$$

for $y<0$. The solution of Eq. (10) that does not diverge at infinity after the replacement $\omega\rightarrow\omega+is$, $s\rightarrow+0$ (which corresponds to external field turned on adiabatically) can be written in the following form:

$$f(z)=1+\frac{C_1}{z}H_{\sqrt{7}}^{(1)}(z)-\frac{3\pi i}{2z}\left(H_{\sqrt{7}}^{(1)}(z)\int_{z_0}^{z}H_{\sqrt{7}}^{(2)}(z')dz'\right.$$

$$\left.+H_{\sqrt{7}}^{(2)}(z)\int_{z}^{\infty}H_{\sqrt{7}}^{(1)}(z')dz'\right), \tag{12}$$

where $z=2\sqrt{3}(\omega/\omega_p)\exp(y/2)$, $z_0=2\sqrt{3}\omega/\omega_p$, $H_{\sqrt{7}}^{(1)}(z)$, and $H_{\sqrt{7}}^{(2)}(z)$ are the Hankel functions. We can find the analytical solution of Eq. (11) for the region $y\ll-1$ only:

$$f(y)=f_m+C_2\exp\left\{\left[\frac{3}{2}\left(1-\frac{\omega^2}{\omega_p^2}\right)\right]^{1/2}y\right\}, \tag{13}$$

where $f_m=E_m/E_{ex}=-\omega^2/(\omega_p^2-\omega^2)$ is the dimensionless field in the bulk region. Taking Eq. (13) as an approximate solution of Eq. (11) in the whole region $y<0$, we can estimate the integration constants C_1 in Eq. (12) and C_2 in Eq. (13) matching the functions $f(y)$ from these equations and their derivatives at $y=0$. We found that this is a reasonable approximation at least for $\omega\ll\omega_p$; numerical solution of Eq. (11) in this case gives only unimportant corrections. The result for the local field outside the metal is shown in Fig. 1. The real part of the dimensionless field $\mathrm{Re}[f(y)]=\mathrm{Re}[E_1(y)/E_{ex}]$ oscillates with y about one. The oscillation amplitude decreases with increasing y and $\mathrm{Re}(f)$ approaches unity at large distances from the metal $y\gg1$. It is more important that the local field $f(y)$ has well developed imaginary part $\mathrm{Im}(f)$ comparable with $\mathrm{Re}(f)$. What this means is an absorption outside the classical metal boundary. Moreover, in the FIR spectral region this absorption is much larger than in the metal itself since the field in the metal much depressed $f(y<0)\sim E_m/E_{ex}\ll1$. The dominant contribution to the absorption gives the region near the plasma resonance point where the local plasma frequency $\omega_p(x)=[N_0(x)/N_i]^{1/2}\omega_p$ is equal to the frequency of the external field ω. We speculate that the effective absorption results from the oscillations excited by the longitudinal external field in the nonuniform electron cloud outside the metal. The energy of the external field goes to the local charge oscillation modes that have a continuous spectrum $\omega_p(x)$ and interfere destructively. Finally the energy is dissipated, in the metal.

Since the field is very small in the metal for $\omega\ll\omega_p$ we can use the approximate boundary condition $f(y=0)=0$ in Eq. (12) to find the constant $C_1=[3\pi iH_{\sqrt{7}}^{(2)}(z_0)/2H_{\sqrt{7}}^{(1)}(z_0)]\int_{z_0}^{\infty}H_{\sqrt{7}}^{(1)}(z)dz-z_0/H_{\sqrt{7}}^{(1)}(z_0)$ explicitly and, therefore, the explicit form for the field in the electron cloud outside the metal. Note that the field $f(y)$ appears to be a universal function of the variable $z=2\sqrt{3}(\omega/\omega_p)\exp(y/2)$ for frequencies much lower than ω_p. We use the thus determined local field to find the absorption Q in a metal particle. Since the total current is constant in the considered plane geometry [see Eq. (8)] the absorption per unit area can be estimated as

$$Q\simeq(1/2)\mathrm{Re}\left[(i\omega/4\pi)E_{ex}^{*}\int_{-a/2}^{\infty}E(x)dx\right].$$

Neglecting the field in the metal we obtain

$$Q\simeq C\frac{\omega R_D E_{ex}^2}{4\pi}, \tag{14}$$

where $C=-\int_{z_0}^{\infty}z^{-1}\mathrm{Im}\,f(z)dz$, and $f(z)$, z_0 are determined in Eq. (12). For $\omega\ll\omega_p$ $(z_0\ll1)$ the factor $C\simeq1.57$ does not depend for all practical purposes, on frequency. Then Eq. (14) predicts the linear frequency dependence for the absorption. Some experiments do agree with this prediction,[1,7,15] other ones do not, indicating stronger, roughly quadratic dependence.[2,6] A wider frequency range is required to make the distinction.

In the common approach, a metal particle is described by a conductivity σ, which does not take into account the spill-out of the electrons. It might be Drude type conductivity $\sigma=\sigma_0/(1-i\omega\tau)$. Then the electric field E_i inside the particle can be estimated as $E_i=3E_{ex}/(2+4\pi i\sigma/\omega)$. Respectively, the classical electric-dipole absorption per unit volume Q_c is $Q_c\simeq9\omega^2|E_{ex}|^2/(32\ \pi^2\sigma_0)$ for $\sigma_0\gg\ \omega,1/\tau$. Therefore, we can estimate the enhancement of the FIR absorption due to surface diffuseness as

$$G\simeq\frac{4\pi a^2Q}{\frac{4}{3}\pi a^3Q_c}=\frac{8\pi C}{3}\frac{R_D}{a}\frac{\sigma_0}{\omega}. \tag{15}$$

For the small particles the relaxation time might be estimated as $\tau\sim a/V_F$ and, respectively, $\sigma_0=\omega_p^2\tau/(4\pi)$

$\simeq \omega_p^2 a/(4\pi V_F)$. Taking into account that $R_D/V_F = (3/2)^{1/2}\omega_p^{-1}$ we can see from Eq. (15) that the enhancement G first increases with a decrease in particle size a; then it saturates at value $G \simeq A\omega_p/\omega$, where $A=(2/3)^{1/2}C \simeq 1.28$. For a typical metal the plasma frequency $\omega_p \sim 10^{16}$ $\sec^{-1}$, therefore for the frequency $\omega \sim 10^{13}$ $\sec^{-1}$ we have the enhancement factor $G \sim 10^3$. This value is in an agreement with experimental results of Kim and Tanner[6] and Lee *et al.*[7]

Up to now we have been considering the unsupported particle in vacuum. The results remain without change, of course, if the surrounding medium is a structureless dielectric continuum. However, it is clear from the previous consideration that the absorption can be very sensitive to the microscopic potential landscape outside of the particle. If so, the effects due to the dielectric host surrounding may be important and cannot be described by the continuous dielectric model. Let us assume, for example, that there is a strongly repulsive potential barrier at the point $x=b(b>0)$, so we can use the boundary condition $j(x=b)=0$ or, equivalently, $E_1(x=b)=E_{ex}$ [see Eq. (8)]. It is easy to show that in this case the field can be expressed in terms of the real Bessel functions instead of the complex Hankel functions appearing in Eq. (12). Respectively, the absorption disappears in the limit $1/\tau \rightarrow 0$. This may give the possible explanation as to why the anomalous absorption by a silver particle in a gelatin matrix has not been found in Devaty-Sievers experiments.[2]

Let us recall that our results have been obtained for the case when the local velocity has the form $V(x) = V_F[N_0(x)/N_i]^{1/2}$, which leads to the exponential decay of the equilibrium electron density tail. Alternatively, one could choose, for example, Thomas-Fermi form $V(x) = V_F[N_0(x)/N_i]^{1/3}$. Then Eqs. (4) yield $N_0 \sim x^{-6}$, i.e., the well-known Thomas-Fermi result for a plane boundary. In this case our model gives the the field distribution $E_1(y)/E_{ex}$, similar to that shown in Fig. 1 with the difference that the point of plasma resonance is shifted farther to the right of the boundary. It can be shown that the absorption in this case is given by Eq. (14) again with almost frequency-independent parameter C of the order of 1.

For macroscopic planar surface the described mechanism should give the additional contribution to the total absorption if the electric field component perpendicular to the surface is nonzero. This requirement is fulfilled, e.g., for surface electromagnetic waves and free-space *p*-polarized incident radiation. In this case, however, the normal electric field on the metal side is small comparing with the parallel field, $|E_\perp/E_\parallel| \sim 1/\sqrt{|\epsilon|} \ll 1$, where $\epsilon = 1+4\pi i\sigma(\omega)/\omega$ is the dielectric function of the metal. Respectively, the absorption is dominated by electric current parallel to the surface within a skin depth δ, making it unlikely that the proposed mechanism could give any measurable effects. The ratio of the absorption given by Eq. (14) to the classical losses due to the Joule heating in this case appears to be of the order of $R_D/\delta \ll 1$. Surface-electromagnetic-wave spectroscopy does not show any anomaly in the absorption indeed.[16]

In summary, we argue that enhanced FIR absorption is a general feature of the isolated metal particles arising due to the interaction of the electron cloud around it with the external field. The simplest possible kinetic model has been constructed to describe this interaction self-consistently. The main result is that the FIR absorption may be anomalously large even for the loss-free particles. The mechanism of the energy absorption in the inhomogeneous loss-free electron gas seems to be close in spirit to Landau damping (phase mixing), and does not put constraints to the particle size, and a character of the electronic scattering. However, the absorption due to this mechanism can be sensitive to the microscopic properties of the dielectric surrounding and in some cases may be completely suppressed. Our simple quasiclassical model certainly cannot reproduce all details of the energy absorption by electron cloud around a small metal particle. Nevertheless, we believe that proposed theory captures qualitatively the main features of this process.

We would like to acknowledge useful discussions with A. N. Lagarkov. This work was supported by the Russian Fund for Fundamental Research under Grant No. 98-02-17628.

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