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Quantum size effects in the optical properties of small metallic particles

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The electric-dipole susceptibility of small metal particles of characteristic dimension L is calculated within the random-phase approximation on the assumption that $k_F^{-1} << L << \lambda$, where λ is the wavelength of the electromagnetic field and k_F the Fermi wave vector for bulk metal. Electron scattering is introduced in a number-conserving relaxation time approximation, and the optical conductivity of a single particle and the absorption coefficient for a suspension of such particles are determined. The matrix elements for cubical particles are sufficiently tractable that the evolution of the optical properties with particle size may be followed down to a metal-insulator transition demonstrated to occur for particle dimensions ($\sim 1/k_F$) consistent with the Ioffe-Regel localization criterion. The far-infrared absorption coefficient is found to diverge as the critical particle size is approached. The surface plasmon is monotonically red-shifted and considerably broadened by Landau damping. Criteria for observing the discrete optical structure in small metallic particles are presented.

I. INTRODUCTION

Optical measurements have traditionally been one of the most direct techniques for observing the properties of matter of small characteristic dimensions. In this context the criterion for smallness is clearly fixed by comparison with the wavelength λ of incident light. Only fairly recently, however, has it been possible to produce samples of small particles (or small structures using, for example, the techniques of semiconductor technology) which are readily characterized and reasonably uniform in size. Moreover, unusual behavior has been predicted and/or observed for a whole host of thermodynamic and transport properties whenever the wavelength of the quantum excitations within such a small particle becomes comparable to its physical dimensions.[1]

We will confine our attention below to the optical properties of a simple model of a small metallic particle system. In Sec. II we will briefly review the classical predictions for the optical properties of a dilute suspension of metallic spheres small in comparison to the wavelength of incident light and remark on the inadequacy of this treatment, particularly in the far infrared, in explaining experimental results. The motivation for considering quantum size effects will be presented in Sec. III, in Secs. IV and V a general random-phase approximation (RPA) calculation for the optical response will be reviewed, and in Sec. VI and succeeding sections the results of this formalism will be applied to a simple particle-in-a-box model for the electrons in a small metal particle, with appropriate simplifying approximations.

We will see that in order to make meaningful comparisons between quantum size effect predictions and experiment, the effects of electron scattering must be carefully introduced. Further, the distribution of particle sizes in real systems must be taken into account. For a narrow enough distribution of particle size the absorption coefficient of the system should exhibit ripples corresponding to smeared-out discrete level structure. In addition, the familiar Mie sphere resonance will be considerably broadened as a consequence of Landau damping in the discrete system. We will also see, however, that quantum electric dipole contributions remain inadequate to explain the observed magnitude of the far-infrared absorption coefficient in such systems. This conclusion is unaltered by inclusion of magnetic dipole (both classical and semiclassical) effects.

II. CLASSICAL ELECTRODYNAMICS OF A SUSPENSION OF SMALL METAL SPHERES

The Mie solution for the scattering and diffraction of light by a single homogeneous sphere pro-

vides a complete description of the "optical properties" of an isolated spherical particle characterized by a dielectric function $\epsilon(\omega)$.[2,3] It is then a straightforward matter to determine, at least in the long-wavelength limit, the optical properties of a dilute collection of such particles embedded in a host medium (the usual experimental configuration) via Lorentz local-field arguments. In the Mie treatment the total field outside a sphere is decomposed into the field of the incident electromagnetic wave and the scattered field. The scattered fields, in turn, for spheres of radius R very small in comparison to the wavelength of incident light, may be expanded in electric and magnetic multipole fields, each of an amplitude depending only on the particle size (through the dimensionless small parameter $qR=2\pi R/\lambda$) and the dielectric constant of the medium composing the sphere and the host medium (assumed for convenience to be a vacuum). For small enough spheres only the lowest multipoles will have physical importance; the scattered fields at distances far from the sphere are those of a point electric dipole of moment

$$p_0^{\rm el}=R^3\left[\frac{\epsilon-1}{\epsilon+2}\right] \tag{1}$$

and a point magnetic dipole of moment

$$p_0^{\rm mag}=(qR)^2\frac{R^3}{30}(\epsilon-1)\ , \tag{2}$$

where we observe that the magnetic term is characteristically reduced by the factor $(qR)^2$, assumed small. Provided ϵ is finite, the amplitude of the $(l+1)$st electric partial wave (i.e., of multipole index l) is of the same order of magnitude as that of the lth magnetic partial wave. On the other hand, if $|\epsilon|\to\infty$ the electric and magnetic partial waves of given l may be comparable.[3] This observation will become important below.

Standard arguments result in the well-known isotropic Lorentz local-field result[4]

$$\vec{\rm E}_{\rm loc}=\vec{\rm E}\Big/\left[1-\frac{4\pi}{3}\frac{N}{\Omega}\alpha\right]\ , \tag{3}$$

where $\vec{\rm E}$ is the applied field, for N identical entities of polarizability α in a volume Ω. Identifying, for a composite medium,

$$\vec{\rm D}_c=\bar{\epsilon}_c\vec{\rm E}_c=\vec{\rm E}_c+4\pi\vec{\rm P}_c\ , \tag{4}$$

where

$$\vec{\rm P}_c=\frac{N}{\Omega}\alpha\vec{\rm E}_{\rm loc}^{\,c}=\frac{N}{\Omega}\vec{\rm p}\ , \tag{5}$$

we find

$$\bar{\epsilon}_c=1+4\pi\frac{N}{\Omega}\alpha\Big/\left[1-\frac{4\pi}{3}\frac{N}{\Omega}\alpha\right]\ , \tag{6}$$

or, using explicitly (1) for the polarizability of a small sphere of dielectric constant ϵ, we find, rewriting slightly,

$$\bar{\epsilon}=\bar{\epsilon}_{\rm MG}=\frac{1+2Z^e}{1-Z^e}\ , \tag{7}$$

where

$$Z^e=\eta\left[\frac{\epsilon-1}{\epsilon+2}\right]=\frac{4\pi}{3}\frac{N}{\Omega}p_0^{\rm el}\ .$$

Here $\eta=(N/\Omega)(4\pi/3)R^3$ is recognized as the fraction of the composite sample volume occupied by the small spheres. The subscript MG identifies the well-known Maxwell-Garnett result,[5] known theoretically to be appropriate[6] for the case of a dilute, random suspension of isolated metal spheres. It is also known to be inadequate, however, when the particles are no longer isolated from one another, or when the host and inclusions enter on a topologically similar footing.[6] There are other ways of deriving the Maxwell-Garnett result, but the one above emphasizes that it is fundamentally a local-field property and suggests directly the procedure for the magnetic dipole case. The symmetry between ϵ and μ in Maxwell's equations means that wherever the electric dipole moment of a small particle $p_0^{\rm el}$ appears we may replace it by $p_0^{\rm mag}$, the corresponding magnetic term, in order to obtain the composite magnetic permeability:

$$\bar{\mu}_c=\bar{\mu}_{\rm MG}=\frac{1+2Z^m}{1-Z^m}\ , \tag{8}$$

$$Z^m=\eta\frac{(qR)^2}{30}(\epsilon-1)\ .$$

This expression (and the entire multipole expansion) only makes sense in the context of small qR, though qR does not actually appear in the electric dipole result (7). If the quasistatic limit is defined as

$$\{\,|q^hR|,|q^iR|,|\bar{q}R|\,\}\ll 1\ ,$$

where q^h and q^i are the (in general complex) wave vectors for propagation in the host and inclusion materials, respectively, and $\bar{q}$ is the effective composite propagation wave vector, then in the absence of clustering of inclusions it may be shown[6] that

the correct composite index of refraction for this geometry is

$$\bar{n}_c=[(\bar{\epsilon}\bar{\mu})_c]^{1/2}\cong(\bar{\epsilon}_{\rm MG}\bar{\mu}_{\rm MG})^{1/2}\ . \tag{9}$$

We shall be concerned in this section primarily with the far-infrared (low-frequency) behavior of a quantity of particular interest experimentally, namely the absorption coefficient α, defined by the attenuation of intensity I of an incident beam through a sample of the composite via

$$I=I_0e^{-\alpha x}\ , \tag{10}$$

where x is the depth into the sample. Evidently for our assumed isotropic homogeneous composite medium

$$\alpha(\omega)=\frac{2\omega}{c}\,{\rm Im}(\bar{\epsilon}\bar{\mu})_c^{1/2}$$
$$\cong\frac{2\omega}{c}\,{\rm Im}(\bar{\epsilon}_{\rm MG}\bar{\mu}_{\rm MG})^{1/2}\ , \tag{11}$$

since the wave vector has the form $\bar{q}=(\omega/c)\bar{n}_c$.

It is customary to assume that the physical properties of matter in a small metallic particle are essentially identical to the bulk. We note, for instance, that even a 50-Å diameter Al sphere contains about 4000 atoms. Much of the experimental data available is for so-called simple metals, i.e., those well described at low frequencies by treating the electrons as nearly free but nevertheless experiencing collisions. We may therefore adopt a Drude model[7] as a reasonable basis for predicting the classical optical properties of small metallic particles, at least for frequencies below the threshold for interband transitions. In the Drude model

$$\epsilon(\omega)=\epsilon_0-\frac{\omega_p^2}{\omega(\omega+i/\tau)}\ , \tag{12}$$

where ω_p is the plasma frequency of the metal, depending only on the average density of conduction electrons and corrected with an optical effective mass if interband effects are important. Here $1/\tau$ is the mean scattering rate for these electrons, and ϵ_0 is the "core polarizability" of the otherwise inert ions. For later comparison we note that the only concession to the *small sphere size* which is occasionally made is to supplement the bulk scattering rate by a term representing (diffuse) surface scattering, via the expression[8]

$$\frac{1}{\tau_{\rm eff}}=\frac{1}{\tau_{\rm bulk}}+\frac{v_F}{R}\ , \tag{13}$$

where v_F is the Fermi velocity (a reasonable estimate of a conduction-electron speed) and R the sphere radius (a reasonable guess as to the mean distance traveled before a typical electron scatters off the surface). The dielectric function in (12) is then explicitly a function of size R. We will have more to say about the simple additivity of these processes later.

From (7)–(9) and (11), supplemented by a choice for $\epsilon(\omega)$, follow all of the optical properties of the composite medium, at least in the quasistatic limit where truncation of the Mie series makes sense. For example, for small η and to lowest order in ω we find

$$\alpha(\omega)=\frac{\eta\omega^2}{c}\left[\frac{9}{4\pi\sigma_{\rm dc}}+\frac{4\pi\sigma_{\rm dc}R^2}{10c^2}\right]\ . \tag{14}$$

Here the first and second terms in the large parentheses are the electric and magnetic dipole contributions, respectively. The static conductivity of the metal component (not the composite) is given in the Drude model by

$$\sigma_{\rm dc}=\frac{\omega_p^2\tau}{4\pi}\ . \tag{15}$$

(We have also replaced q by ω/c). As noted by Tanner *et al.*,[9] Granqvist *et al.*,[10] and Stroud and Pan,[11] the magnetic dipole (eddy current) term has the same frequency dependence as the electric, but rapidly dominates the electric absorption as the particle size increases. As an example, we note that for Al at room temperature the two terms are equal in magnitude at $R=6$ Å, but by $R=18$ Å the magnetic term accounts for 90% of the total absorption coefficient. If we include the surface scattering correction (13), the corresponding figures are 32 and 55 Å.

The numerical predictions of Eq. (14) still fall a factor of 10^3-10^4 below what is observed experimentally.[9,10,12] A number of mechanisms have been proposed to explain this excess low-frequency absorption. These include absorption due to dielectric losses in amorphous oxide coatings on long chains and clumps of metallic particles,[13,14] absorption due to the clumping itself,[14,15] and the direct excitation of bulk phonons by the unscreened applied field acting on surface ions.[16] While the quadratic frequency dependence predicted by (14) is in rough accord with experiment, almost all possible explanations give such a dependence; even a very different process, photon-assisted electron hopping between small particles would give rise to a dependence[12,17]

$$\alpha(\omega)\sim\omega^2\left[\ln\frac{(\text{const})}{\omega}\right]^4,$$

which does not depart radically from the leading ω^2 dependence.[18]

With this section as background we proceed in Sec. III to a quantum mechanical treatment of the problem, focusing our attention on the properties of a single, isolated metallic particle.

III. QUANTUM SIZE EFFECTS

The possibility of quantum size effects in the optical properties of small metallic particles has attracted considerable theoretical attention.[18–30] A few remarks about why a quantum treatment will be necessary, at least for small enough particles, and what qualitative features we expect to emerge, are appropriate.

First, within the single-particle approximation, one could imagine solving for the eigenstates of free electrons subject only to the constraint that they remain within a finite volume. The energy levels of such a small particle will then be discrete and the small energy difference (the "gap") between the highest occupied level (the "Fermi level") and the lowest unoccupied level will mean that, in principle, the particle as a whole will behave as a large "atom." At zero frequency it will assume the characteristics of an insulator. The use of any bulk concept like a conductivity is suspect, of course, when applied to a small enough system. We will make our definition more precise below, however.

In practice even a rather small particle ($R\sim 20$ Å) has thousands of electrons and we will assume that, as in the bulk, conduction electrons scatter from impurities, and (at finite temperatures) from phonons. (There is some evidence that the metallic character of a small particle will persist down to clusters of a few hundred atoms[31]; for extremely small particles we clearly expect a metal-insulator transition to occur. We will have more to say about this matter below.) Hence, unlike the case for an atom, we qualitatively expect there to remain at least some means of dissipation down to low frequencies, with an associated finite dc "conductivity." This conductivity will in general be much reduced with respect to the bulk metallic value. An important consequence of a reduced dc conductivity is an enhanced electric dipole contribution to the far-infrared absorption coefficient (14), which depends inversely on $\sigma_{\rm dc}$.

In the treatment below our approach will be to (i) calculate the *polarizability* $\alpha(\vec{q},\omega)$ for a general bounded quantum system in the $q=0$ limit within an approximation of *diagonal response,* (ii) use the relation between the polarizability and dielectric function to extract $\epsilon(\omega)$, and (iii) introduce the effects of electron scattering in a locally number-conserving relaxation time approximation in order to make detailed predictions about the optical properties and frequency-dependent conductivity of small metallic particles. As usual in a single-particle picture, the entities responsible for the processes we will calculate will be assumed to be *quasiparticles.* It is clear that such an interpretation is necessary, as it is in bulk metals, when we observe that the Coulomb energy of two electrons in a sphere of radius $R\sim 20$ Å is of order $e^2/R\approx 0.05$ Ry. We will lump this energy together with the large negative energy usually implicitly assigned to jellium (in order to bind electrons within a finite box) in the calculation to be presented below.

IV. FORMALISM (REF. 32)

The Hamiltonian of a system of electrons (charge $-e$) in the presence of a semiclassical electromagnetic field characterized by vector potential $\vec{A}(\vec{r},t)$ and scalar potential $\phi(\vec{r},t)$ is

$$H=\frac{1}{2m}\left[\hat{\vec{p}}+\frac{e}{c}\vec{A}\right]^2+V(\vec{r})+\phi(\vec{r}),\tag{16}$$

where $V(\vec{r})$ is the potential in the absence of an applied field. If we are interested in *optical* properties we may neglect the term in A^2 and treat the terms linear in $\vec{A}$ as a perturbation. We are at liberty[32] to select a gauge where $\phi\equiv 0$. It is important to observe that in a metallic system it is the *screened* (not externally applied) field to which the independent electrons respond. In a linear-response treatment, however, we may extract the quantity of interest by forming the "ratio" of response to driving field, so that we may simply reinterpret $\vec{A}(\vec{r},t)$ as the effective local screened field which will, however, no longer be purely transverse even if the incident field is. We may then write

$$H=\left[\frac{\hat{p}^2}{2m}+V(\vec{r})\right]+\left\{\frac{e}{2mc}(\hat{p}\cdot\vec{A}+\vec{A}\cdot\hat{p})\right\}$$

$$\equiv[H_0]+\{H_1\},\tag{17}$$

where we regard H_1 as a small perturbation on the states $|i\rangle$ of H_0. We then calculate the current induced by an applied electromagnetic field. Let $\hat{\rho}$ be the density matrix appropriate to a system described by a Hamiltonian H in thermal equilibrium, and defined by

$$\hat{\rho} \equiv \{ \exp[\beta(\hat{H}-\mu)]+1 \}^{-1} \tag{18}$$

for $\beta=(k_B T)^{-1}$. For any eigenstate $|i\rangle$ of $\hat{H}$

$$\begin{aligned}\hat{\rho}|i\rangle &= \{ \exp[\beta(\varepsilon_i-\mu)]+1 \}^{-1}|i\rangle \\ &= f_i|i\rangle ,\end{aligned} \tag{19}$$

where f_i is the Fermi-Dirac occupation factor for that state. For a statistical ensemble, then, the expectation value of an operator $\hat{0}$ is

$$\langle \hat{0} \rangle = \mathrm{Tr}\{\hat{\rho}\hat{0}\} = \sum_{ij} \langle i|\hat{\rho}|j\rangle\langle j|\hat{0}|i\rangle . \tag{20}$$

To linear order in an applied perturbation we may write

$$\hat{\rho} \approx \hat{\rho}^{(0)} + \hat{\rho}^{(1)} , \tag{21}$$

where $\hat{\rho}^{(0)}$ is the density matrix of the system described by H_0 and $\hat{\rho}^{(1)}$ is the perturbation in $\hat{\rho}$ due to H_1. In general $\hat{\rho}$ obeys the Liouville equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H},\hat{\rho}] , \tag{22}$$

from which we may write

$$i\hbar \frac{\partial \hat{\rho}^{(1)}}{\partial t} = [H_1,\hat{\rho}^{(0)}] + [H_0,\hat{\rho}^{(1)}] , \tag{23}$$

where we have (i) substituted (17) and (21) into (22), (ii) subtracted the Liouville equation appropriate to H_0 alone from both sides, and (iii) neglected the higher-order term $[H_1,\hat{\rho}^{(1)}]$. Assuming response at the same frequency as the perturbation, taken to be $\exp[-i(\omega+i\eta)t]$ where $\exp(\eta t)$ adiabatically switches on the perturbation from $t=-\infty$, we may evaluate the matrix element to find

$$\langle i|\hat{\rho}^{(1)}|j\rangle = \frac{(f_i-f_j)}{\varepsilon_i-\varepsilon_j-\hbar\omega-i\eta}\langle i|H_1|j\rangle , \tag{24}$$

where $|i\rangle$ and $|j\rangle$ are eigenstates of H_0. [Henceforth we will omit the $-\eta$, although for choice of branch or contour ω will always be assumed to be $(\omega+i\eta)$, until we discuss broadening later.] For H_1 in (17) we select $\vec{A}(\vec{r},t)$ to be monochromatic[33]

$$\vec{A} = \vec{A}_0 \exp[i(\vec{q}\cdot\vec{r}-\omega t-i\eta t)] . \tag{25}$$

Then

$$\begin{aligned}\langle i|\hat{\rho}^{(1)}|j\rangle = \frac{e}{mc}\frac{(f_i-f_j)}{(\varepsilon_{ij}-\hbar\omega-i\eta)} \\ \times\vec{A}_0\cdot\left[\langle i|e^{i\vec{q}\cdot\vec{r}}\vec{p}|j\rangle + \frac{\hbar\vec{q}}{2}\langle i|e^{i\vec{q}\cdot\vec{r}}|j\rangle\right] .\end{aligned} \tag{26}$$

The final term in large parentheses appears because for our choice of gauge $\vec{\nabla}\cdot\vec{A}=i\vec{q}\cdot\vec{A}\neq 0$ in general.

We may next compute the current induced by the perturbation $\hat{H}_1$. The current operator is given by

$$\hat{\vec{j}} = \frac{-e}{2m}(\hat{n}\hat{\vec{p}}_c + \hat{\vec{p}}_c\hat{n}) , \tag{27}$$

where

$$\hat{\vec{p}}_c \equiv \hat{\vec{p}} + \frac{e}{c}\vec{A} \quad \text{and} \quad \hat{n} \equiv \delta(\vec{r}-\hat{\vec{r}}) . \tag{28}$$

The expectation value of $\hat{\vec{j}}$ is

$$\begin{aligned}\vec{j}_{\mathrm{ind}}(\vec{r},t) &= \mathrm{Tr}\{\hat{\rho}\hat{\vec{j}}\} \\ &\cong \mathrm{Tr}\{\hat{\rho}^{(0)}\hat{\vec{j}}^{(1)} + \hat{\rho}^{(1)}\hat{\vec{j}}^{(0)}\}\end{aligned}$$

with

$$\hat{\vec{j}}^{(0)} = \frac{-e}{2m}[\hat{\vec{p}}\delta(\vec{r}-\hat{\vec{r}}) + \delta(\vec{r}-\hat{\vec{r}})\hat{\vec{p}}] \tag{29}$$

and

$$\hat{\vec{j}}^{(1)} = \frac{-e^2}{mc}\vec{A}\delta(\vec{r}-\hat{\vec{r}}) .$$

Let $\varepsilon_{ij}=\varepsilon_i-\varepsilon_j$. We now perform the trace and Fourier transform the resulting expression for the total induced current in a volume Ω to obtain

$$\begin{aligned}\vec{j}_{\mathrm{ind}}(\vec{k},\omega) = \frac{-e^2}{\Omega mc}\vec{A}_0\sum_i f_i\langle i|e^{i(\vec{q}-\vec{k})\cdot\vec{r}}|i\rangle \\ -\frac{e^2}{\Omega m^2 c}\sum_{ij}\frac{(f_i-f_j)}{\varepsilon_{ij}-\hbar\omega}[\langle i|e^{i\vec{q}\cdot\vec{r}}\vec{A}_0\cdot\hat{\vec{p}}|j\rangle + \tfrac{1}{2}\hbar\vec{q}\cdot\vec{A}_0\langle i|e^{i\vec{q}\cdot\vec{r}}|j\rangle] \\ \times[\langle j|e^{-i\vec{k}\cdot\vec{r}}\hat{p}|i\rangle - \tfrac{1}{2}\hbar\vec{k}\langle j|e^{-i\vec{k}\cdot\vec{r}}|i\rangle] ,\end{aligned} \tag{30}$$

where "off-diagonal response," i.e., at wave vectors other than that of the applied field, is now evident.

V. DIAGONAL RESPONSE AND THE DIELECTRIC FUNCTION

We shall adopt the viewpoint that for dynamical effects in small particles it is the *discreteness* of the energy levels, and not the associated inhomogeneous charge distribution, which is important. We further note that the scale of inhomogeneity of the electron density near a surface is of order $1/k_F$, where k_F is the Fermi wave vector appropriate to the electron density. Provided, therefore, that the characteristic dimensions of the small particle are large in comparison to $1/k_F$, an approximation which takes the unperturbed electronic system as *homogeneous* (although finite) should be acceptable. This assumed homogeneity, together with deliberate neglect of surface effects, will constitute our definition of an approximation known as *diagonal response.* It asserts that the system responds only at the wave vector of the applied field. For atomic systems, diagonal response is assumed almost without exception,[34,35] and corresponds to the use of the multipole expansion with a constant local field, as discussed below.

With the approximation $\vec{k}=\vec{q}$ in (30) we then find

$$\vec{j}_{\rm ind}(\vec{q},\omega)=\frac{-Ne^2}{mc\Omega}\vec{A}(\vec{q},\omega) - \frac{e^2}{m^2c\Omega}\sum_{ij}\frac{(f_i-f_j)}{\varepsilon_{ij}-\hbar\omega}\{\vec{A}(\vec{q},\omega)\cdot[\langle i|e^{i\vec{q}\cdot\vec{r}}\hat{\vec{p}}|j\rangle+\tfrac{1}{2}\hbar\vec{q}\langle i|e^{i\vec{q}\cdot\vec{r}}|j\rangle]\} \times(\langle j|e^{-i\vec{q}\cdot\vec{r}}\hat{\vec{p}}|i\rangle-\tfrac{1}{2}\hbar\vec{q}\langle j|e^{-i\vec{q}\cdot\vec{r}}|i\rangle)\,, \tag{31}$$

where we have used $\sum_i f_i=N$, the total electron number. We recognize the first term as the "diamagnetic current." The physical picture we have in mind is an external transverse plane wave of wave vector $\vec{q}$ incident on a particle small in comparison with the wavelength. For a small enough particle we may take the $q\to 0$ limit to find

$$\lim_{\vec{q}\to 0}\vec{j}_{\rm ind}(\vec{q},\omega)=\frac{-e^2}{mc}\frac{N}{\Omega}\vec{A}(\omega)-\frac{e^2}{\Omega m^2c}\sum_{ij}\frac{(f_i-f_j)}{\varepsilon_{ij}-\hbar\omega}[\vec{A}(\omega)\cdot\langle i|\hat{\vec{p}}|j\rangle]\langle j|\hat{\vec{p}}|i\rangle\,. \tag{32}$$

This limit, in which the momentum matrix element alone survives, corresponds to the complete neglect of the spatial variation of the electromagnetic field across the region of interest. It is the familiar (electric) dipole approximation. It neglects the rapid oscillations of electrodynamic quantities near the surface. In our gauge $\vec{E}(\omega)=(i\omega/c)\vec{A}(\omega)$; we will be interested in the transverse response of the system to the transverse electric field of an incident light wave. In the long-wavelength limit this is equivalent to the longitudinal response of the system to a longitudinal field.[32,36] By forming the scalar product of $\vec{j}_{\rm ind}$ and $\vec{E}(\omega)$ we may identify the optical conductivity

$$\sigma(\omega)=i\left[\frac{e^2}{m\omega}\frac{N}{\Omega}+\frac{e^2}{\Omega m^2\omega}\times\sum_{ij}\frac{(f_i-f_j)}{\varepsilon_{ij}-\hbar\omega}|\langle i|\hat{p}_E|j\rangle|^2\right]. \tag{33}$$

Using the general relation

$$\epsilon(\omega)=1+i4\pi\sigma(\omega)/\omega \tag{34}$$

we then have

$$\epsilon(\omega)=\left[1-\frac{\omega_p^2}{\omega^2}\right] - \frac{4\pi e^2}{\Omega m^2\omega^2}\sum_{ij}\frac{(f_i-f_j)|\langle i|\hat{p}_E|j\rangle|^2}{\varepsilon_{ij}-\hbar\omega}\,, \tag{35}$$

where $\hat{p}_E$ denotes the component of the momentum operator along the applied field. We have also defined $\omega_p^2=4\pi e^2(N/\Omega)/m$.

This result is manifestly of the form of free-electron behavior [the first term in (35)] plus corrections falling off faster than $1/\omega^2$ for high frequencies. The corrections, due to the nontranslational invariance of the system, will vanish for an infinite free-electron metal. It will be con-

venient to rewrite (35) via a relabeling of the contribution from the term f_j; interchanging i and j for this term we combine it with that from f_i to find

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2} -\frac{8\pi e^2}{\Omega m^2\omega^2}\sum_{ij}\frac{f_i\epsilon_{ij}\,|\langle i|\hat{p}_E|j\rangle|^2}{\varepsilon_{ij}^2-\hbar^2\omega^2} . \tag{36}$$

We will be concerned with systems small enough that the discreteness of the eigenvalues will be important. We may thus perform a low-frequency expansion

$$\epsilon(\omega)=\left\{1-\frac{8\pi e^2\hbar^2}{\Omega m^2}\sum_{ij}\frac{f_i\,|p_{ij}|^2}{\epsilon_{ij}^3}\right\} -\frac{\omega_p^2}{\omega^2}\left[1+\frac{8\pi e^2}{\Omega m^2\omega_p^2}\sum_{ij}\frac{f_i\,|p_{ij}|^2}{\varepsilon_{ij}}\right]+\cdots$$

$$=\{\epsilon_0\}-\frac{\omega_p^2}{\omega^2}\frac{m}{m^*}+O(\omega^2) . \tag{37}$$

In the theory of the optical properties of crystalline metals[32,36,37] one would normally identify ϵ_0 as the "core polarizability" of the metal and the terms in large curly brackets as the optical effective mass reflecting the presence of a periodic potential. At all frequencies the contributions to $\epsilon(\omega)$ may be decomposed into "intraband" [the first two terms in (37)] and "interband" (the rest). For a small system with genuinely discrete levels we may prove that there is no continuous (intraband) contribution by demonstrating that the effective mass m/m^* vanishes; we use the well-known Thomas-Reiche-Kuhn sum rule[38,39]

$$\frac{2}{m}\sum_j\frac{|p_{ij}|^2}{\varepsilon_{ij}}=-1 , \tag{38}$$

where i and j denote *all* the quantum numbers of a system, and the matrix elements are summed over all states j. Hence the quantity in square brackets in (37) is $[1-\sum_i f_i/N=0]$, allowing us to rewrite ϵ as

$$\epsilon(\omega)=1-\frac{8\pi e^2\hbar^2}{\Omega m^2}\sum_{ij}\frac{|p_{ij}|^2 f_i}{\varepsilon_{ij}(\varepsilon_{ij}^2-\hbar^2\omega^2)} , \tag{39}$$

a well-known result.[40] This derivation is given to emphasize the fact that it results from a nontrivial approximation, that of diagonal response in the electric dipole limit. A second trivial consequence of (38) is the result

$$\lim_{\omega\to\infty}\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2} , \tag{40}$$

i.e., all electrons behave as free electrons for sufficiently high frequencies.

Finally, it is important to remark that any RPA-type calculation (such as the one here) gives response to the *local,* i.e., screened, field[36]:

$$\epsilon_{\rm RPA}=1+4\pi\chi_{\rm RPA} . \tag{41}$$

With respect to the applied, external field[20]

$$\chi_{\rm ext}=\chi_{\rm RPA}\Big/\left[1+\frac{4\pi}{3}\chi_{\rm RPA}\right] , \tag{42}$$

so that the usual local-field correction must be made. The polarizability of a uniform sphere of a medium characterized by $\epsilon_{\rm RPA}=\epsilon$ is thus

$$\alpha=R^3\left[\frac{\epsilon-1}{\epsilon+2}\right] . \tag{43}$$

In our context this means that one could perform an RPA calculation for ϵ of a system of planar symmetry, exhibiting the appropriate bulk plasmon, and merely by using the known classical boundary conditions on the applied and local fields (42), or the Mie theory result (7), be assured that the surface plasmon will be recovered when the denominator of (43) vanishes. This will be our approach below.

VI. THE PARTICLE-IN-A-CUBE MODEL

We are specifically interested in small metallic particles; if we adopt the jellium model we may select particle-in-a-box wave functions as reasonable states

$$\psi_i=\psi_{mnp}=\left[\frac{8}{abc}\right]^{1/2}\sin\frac{m\pi x}{a}\sin\frac{n\pi y}{b}\sin\frac{p\pi z}{c} ,$$

$$\{m,n,p\}=1,2,3,\ldots \tag{44}$$

$$\varepsilon_i=\frac{\hbar^2}{2m}\pi^2\left[\frac{m^2}{a^2}+\frac{n^2}{b^2}+\frac{p^2}{c^2}\right] .$$

Here we have assumed the box to be rectangular, of dimensions $a\times b\times c$; although the states for a three-dimensional infinitely high spherical well

may be explicitly written down in terms of spherical Bessel functions,[21] their matrix elements are very cumbersome to work with in general. These would obviously be more appropriate to the experimentally occurring collections of small roughly spherical particles; our expectation is that the energy and general behavior of, for example, a cube (to which we will specialize) and a sphere will differ only by geometrical factors of the order of 1. We will see this hope borne out several times below, wherever analytic results for spheres exist for comparison.

Although we will be careful to show that with the procedure to be followed below the detailed shape of the particle will not much matter, we part company with the arguments of Kubo[41] that microscopic surface roughness will enormously reduce the degeneracy of a level for a highly symmetrical particle (for a sphere, the m degeneracy of a state of given l; for a box, the degeneracy due to quantum numbers for directions perpendicular to the electric field). We will see below that the optical features which emerge from our treatment will occur for energies of the order of the gap, $\hbar\omega \sim \varepsilon_F/N^{1/3}$ (where ε_F is the Fermi energy and N the number of electrons in the particle), not at the enormously different value $\sim \varepsilon_F/N$ predicted by Kubo. We shall see that in our model a careful accounting of the degeneracy will give rise to, for example, a metal-insulator transition for small enough particles—a phenomenon not readily predicted on the basis of the Kubo arguments.

We now take for convenience the applied and local fields to lie in a direction $\hat{x}$ normal to one of the box faces, such that the dimension along the field is a. Then

$$|\langle i|\hat{p}_x|j\rangle|^2 = \frac{8\hbar^2}{a^2}\frac{m^2 m'^2}{(m'^2-m^2)^2} \times[1-(-1)^{m+m'}]\delta_{nn'}\delta_{pp'}, \quad (45)$$

where $|j\rangle$ is labeled by (m',n',p'). As $a\to\infty$, corresponding to a bulk free-electron metal, the matrix element vanishes, reflecting the fact that a free electron cannot conserve momentum and energy by absorbing a photon. For finite a the particle walls break the translational invariance of free space. The initial and final states in the electric dipole limit must differ in parity.

To simplify the computation of $\epsilon(\omega)$ via (39) we observe that the transverse quantum numbers (n,p) and box dimensions are essentially irrelevant since they uncouple from the strong frequency dependence of $\epsilon(\omega)$. Hence we take the dimensions b and c to be large enough that the *sums* over (n,p) may be replaced by *integrals*. In particular, we make the substitution

$$\sum_{n,p=1}^{\infty}\Theta\left[\varepsilon_F-\frac{\hbar^2}{2m}\pi^2\left[\frac{m^2}{a^2}+\frac{n^2}{b^2}+\frac{p^2}{c^2}\right]\right] \to \frac{bc}{a^2}\frac{\pi}{4}(m_c^2-m^2)\Theta(m_c^2-m^2), \quad (46)$$

where we have (i) assumed a well-defined Fermi level exists, of energy ε_F equal to the bulk metallic value, (ii) assumed the zero-temperature (Heaviside step function) form for the Fermi occupation factor for noninteracting electrons, and (iii) identified $m_c = k_F a/\pi$. The factor of $\frac{1}{4}$ comes from the restriction of (m,n,p) to positive integers.

We will refer to the geometrical entity corresponding to the substitution (46) as a "cube." The approximation preserves the important dependence on discrete energies associated with quantum numbers parallel to the applied field. We will see below how well the approximation fares. Moreover, it will be convenient for computational purposes to quantize the particle dimension a in units of π/k_F. Since this quantity is typically ~ 3 Å and authentically small particles usually have $a \gtrsim 20$ Å, this artifice is not expected to have significant effects.

The approximations above result in enormous simplification in (39). We find

$$\epsilon(x) = 1+\left[\frac{4}{\pi}\right]^4\frac{a}{a_0}\sum_{m=1}^{m_c}m^2(m_c^2-m^2)\sum_{m'=1}^{\infty}\frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)^3[(m'^2-m^2)^2-x^2]}, \quad (47)$$

where

$$x = \hbar\omega\Big/\left[\frac{\hbar^2}{2m}\frac{\pi^2}{a^2}\right], \quad m_c = \frac{k_F a}{\pi}(=\text{integer}), \quad (48)$$

and a_0 is the Bohr radius.

The behavior of (47) is evaluated in a straightforward manner in certain limits. In the limit of high frequency [using the identities (A12) and

(A23) of the Appendix]

$$\lim_{\omega\to\infty}\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}\left[1-\frac{3}{4m_c}-\frac{1}{4m_c^2}\right]. \tag{49}$$

One of the prices we pay for the approximation (46) is now evident: There is a very weak deviation from the (correct) limiting behavior (40) or, alternatively, a weak violation of the f-sum rule. For an Al sphere of 25-Å radius (experimentally quite small) a cube of equivalent volume has $m_c\approx 22$, resulting in about a 3% deviation from (40). (A method for enforcing the sum rule has recently been suggested by Cini.[42] For the infinite potential case [with the same approximation as embodied in (46)] the variable m' is integrated (rather than summed) and a cutoff is introduced whose purpose is to ensure that the sum rule is exactly satisfied. One result of this calculation is an oscillation in the position of the surface plasmon with particle size which is superimposed on a general shift (toward the blue) as particle size is reduced. Cini also treats the finite-well case.)

For low frequencies, on the other hand, we find (see the Appendix)

$$\begin{aligned}\lim_{\omega\to 0}\epsilon(\omega)&=\epsilon_0+O(\omega^2)\\&=1+\left[\frac{4}{\pi}\right]^4\frac{a}{a_0}\frac{\pi^2}{1536}\left[15m_c^2\left[S_4-\frac{1}{m_c^2}S_2\right]+\pi^2 m_c(1-m_c S_2)\right]+O(\omega^2),\\ S_n&=\sum_{m=1}^{m_c}\frac{1}{m^n}.\end{aligned} \tag{50}$$

For large m_c these sums become asymptotic series in $1/m_c$ and Bernouilli numbers; we find

$$\begin{aligned}\lim_{m_c\to\infty}\{\lim_{\omega\to 0}[\lim_{q\to 0}\epsilon(\vec{q},\omega)]\}&=1+\left[\frac{k_F a_0}{3\pi}\right]\left[\frac{a}{a_0}\right]^2\\&=1+0.1061(k_F a_0)\left[\frac{a}{a_0}\right]^2.\end{aligned} \tag{51}$$

In a calculation very similar to ours, but in the q (rather than the ω) domain, Cini and Ascarelli[24] found for cubes

$$\begin{aligned}\lim_{m_c\to\infty}\{\lim_{q\to 0}[\lim_{\omega\to 0}\epsilon(\vec{q},\omega)]\}&=1+\left[\frac{2}{\pi}\right]^5(k_F a_0)\left[\frac{a}{a_0}\right]^2\\&=1+0.1046(k_F a_0)\left[\frac{a}{a_0}\right]^2.\end{aligned} \tag{52}$$

Since in general these limits are not interchangeable, it is remarkable that they agree so well in this case. We will see below that for large m_c the gap for our cubes, i.e., the energy of the lowest allowed optical transition, is $\Lambda\sim 2\varepsilon_F/m_c$, so that our result (51) may be rewritten

$$\epsilon_0=1+\left[\frac{\pi^2}{4}\right]\left[\frac{\hbar\omega_p}{\Lambda}\right]^2, \tag{53}$$

which is precisely of the form expected for an insulating system, e.g., an intrinsic semiconductor.[43]

It is quite instructive to compare our result (51) with the well-known result of Gor'kov and Eliashberg,[19] who found for large sphere radius

$$\lim_{m_c\to\infty}[\lim_{\omega\to 0}\epsilon^{\text{sphere}}(\omega)]=1+\left[\frac{4}{5\pi}\right](k_F a_0)\left[\frac{R}{a_0}\right]^2. \tag{54}$$

In terms of the equivalent volume sphere radius $\bar{R}$ (which we will use below) the two results are

$$\begin{aligned}\epsilon_0^{\text{sphere}}&=1+0.2546(k_F a_0)(R/a_0)^2,\\ \epsilon_0^{\text{cube}}&=1+0.2757(k_F a_0)(\bar{R}/a_0)^2,\end{aligned} \tag{55}$$

so that the geometrical distinction[44] between a sphere and a cube is indeed a factor $O(1)$. From the form of (54) it is clear that the polarizability of a small sphere very rapidly approaches that of an infinitely conducting sphere: R^3 [see Eq. (43)].

VII. QUASICONTINUOUS LIMIT

To anticipate some of the effects we expect to emerge from a full calculation of $\epsilon(\omega)$, and to make contact with the work of Kawabata and Kubo,[21] we will consider a small particle yet with

all dimensions large enough that sums may be replaced by integrals. We will also consider the case of a thin slab—a box two of whose dimensions (here those perpendicular to the applied field) are infinite. To find the effective mass for a thin slab of thickness a, for the discrete m case we must reevaluate (37). The approximation (46) becomes exact for slabs, and using the same identities as before we find

$$\left.\frac{m^*}{m}\right|_{\text{slab}} = 4m_c \Big/ \left[3+\frac{1}{m_c}\right] . \tag{56}$$

The limit (40) is obeyed identically. Rather than pursue further the discrete case, we replace the m sums by integrals. Since in this context "cubes" and "slabs" coincide, we find

$$\epsilon_{\text{qc}}(\omega)=1-\frac{\omega_p^2}{\omega^2}+\left[\frac{e^2}{2a_0}\right]\left[\frac{8}{\pi\hbar\omega}\right]^2\frac{1}{(a/a_0)}\int_0^{\varepsilon_F}d\varepsilon(\varepsilon_F-\varepsilon)\sqrt{\varepsilon}\int_0^{\infty}\frac{d\varepsilon'\sqrt{\varepsilon'}}{(\varepsilon'-\varepsilon)[(\varepsilon'-\varepsilon)^2-\hbar^2\omega^2]} , \tag{57}$$

where we have set $(\hbar^2/2m_e)\,(\pi^2m^2/a^2)=\varepsilon$ (similarly for m') and observed that the average value of $[1-(-1)^{m+m'}]$ is one. The subscript qc denotes quasicontinuous, and m_e is the electron mass. The free-electron density of states form of the integrands is evident; using the identities

$$\frac{1}{x^2-a^2}=\frac{1}{2a}\left[\frac{1}{x-a}-\frac{1}{x+a}\right], \qquad \frac{1}{z-b\mp i\eta}=P\left[\frac{1}{z-b}\right]\pm i\pi\delta(z-b) \tag{58}$$

and the definition

$$\text{Re}\,\sigma(\omega)=\frac{\omega}{4\pi}\,\text{Im}\,\epsilon(\omega) , \tag{59}$$

we find

$$\text{Re}\,\sigma_{\text{qc}}=\frac{8}{\pi^2}\frac{1}{(a/a_0)}\frac{[f(\Omega)-\Theta(1-\Omega)f(-\Omega)]}{\Omega^3}\ \text{Ry}/\hbar , \tag{60}$$

where

$$f(x)=\frac{1}{2}\left[1+\frac{x}{2}\right]\left[\left[1+\frac{x}{2}\right]\sqrt{1+x}-\frac{x^2}{2}\ln\left[\frac{\sqrt{1+x}+1}{\sqrt{|x|}}\right]\right]-\frac{(\sqrt{1+x})^3}{3}, \qquad \Omega=\frac{\hbar\omega}{\varepsilon_F} . \tag{61}$$

For the limiting cases we find for cubes (in Ry/$\hbar$)

$$\frac{a}{a_0}\text{Re}\,\sigma_{\text{qc}}(\omega)=\begin{cases}\dfrac{32}{15\pi^2}\dfrac{1}{\Omega^{5/2}}=\dfrac{0.2162}{\Omega^{5/2}}, & (\Omega\gg 1)\\[2ex] \dfrac{4}{\pi^2}\dfrac{1}{\Omega^2}=\dfrac{0.4053}{\Omega^2}, & (\Omega\ll 1)\end{cases} \tag{62}$$

while Kawabata and Kubo, performing the calculation for spheres, find

$$\frac{R}{a_0}\text{Re}\,\sigma_{\text{qc}}(\omega)=\begin{cases}\dfrac{32}{5\pi^4}\dfrac{1}{\Omega^{5/2}}=\dfrac{0.0657}{\Omega^{5/2}}, & (\Omega>>1)\\[2ex] \dfrac{16}{\pi^4}\dfrac{1}{\Omega^2}=\dfrac{0.1643}{\Omega^2}, & (\Omega\ll 1)\end{cases} \tag{63}$$

Once again we find differences only $O(1)$ between the behavior of a sphere and of a cube; our results (60) and (62) agree with those of Ruppin and Yatom for slabs.[28]

The result (60) (though it is not satisfactory for realistic purposes since it diverges for low frequencies and neglects broadening) is a clear indication of the essential $1/a$ dependence of small-particle effects. More interestingly, we note that provided $1/\tau<<\omega<<\varepsilon_F/\hbar$, Re $\sigma(\omega)$ has the same form as that arising from the Drude result (12), with

$$\left.\frac{1}{\tau_{\text{eff}}}\right|_{\text{qc}}^{\text{cube}}=\tfrac{3}{2}v_F/a=0.931\,v_F/\bar{R} , \tag{64}$$

i.e., precisely the form of the "surface-scattering" contribution to (13) above. Thus Re $\sigma(\omega)$ behaves,

even in the absence of explicit sources of dissipation, as a bulk free-electron metal with a *surface-scattering* rate (64). Since the Mie sphere resonance roughly obeys the inequalities above we conclude (as do Kawabata and Kubo) that, because of Landau damping of the surface-plasmon collective excitation,[21] the surface plasmon will acquire, even in the absence of other means of damping, a width given roughly by (64) above. We expect the more complete discrete treatment below also to result in such damping of the sphere resonance. We now consider the procedure for introducing the effects of an electronic lifetime into our result (47).

VIII. BROADENING

Because we have anticipated that the dc conductivity of a small metal particle will be reduced with respect to the bulk value, it will be essential to introduce broadening rather carefully. The usual RPA prescription for introducing a finite relaxation time τ is to replace the infinitesimal adiabatic switching-on rate $1/\eta$ [see (24) above] with the mean scattering rate $1/\tau$. As noted by Mermin[45] this replacement $\omega \rightarrow (\omega + i/\tau)$ does not conserve local electron number, i.e., the equation of continuity is locally violated. Mermin suggested a method for free electrons which overcomes this difficulty: We shall adapt it to the particle-in-a-box states used above. The Mermin scheme may be summarized as follows. (i) Introduce in the density-matrix definition a local chemical potential shift $\delta\mu(\vec{r})$ which provides the extra degree of freedom necessary to conserve particle number locally; (ii) insert a corresponding (now τ-dependent) term in the equation of motion for $\hat{\rho}^{(1)}$ which relaxes it to the local (rather than the uniform) equilibrium distribution

$$\hat{\rho}_{\text{loc}} = \{\exp[\beta(\varepsilon - \mu - \delta\mu)] + 1\}^{-1} , \tag{65}$$

(iii) use the equation of continuity for the number current to close the set of equations. We are interested in the $q = 0$ limit of the dielectric function for small enough particles. In this limit the Mermin result may be written

$$\begin{aligned} \text{Re}\,\epsilon_{\text{corr}}(\omega) &= \text{Re}\,\epsilon(\bar{\omega}) - \frac{1}{\omega\tau}\text{Im}\,\epsilon(\bar{\omega}) , \\ \text{Im}\,\epsilon_{\text{corr}}(\omega) &= \text{Im}\,\epsilon(\bar{\omega}) \\ &\quad + \frac{1}{\omega\tau}[\text{Re}\,\epsilon(\bar{\omega}) - 1] , \end{aligned} \tag{66}$$

where the subscript corr means "corrected to be number conserving," and $\bar{\omega} = \omega + i/\tau$. Garik and Ashcroft[46] have examined in detail the implications of the full number-conserving result in simple crystalline metals. Generally, the explicit corrections are small for bulk metals. This is so largely for two reasons. (a) In genuine bulk metals there is always a continuous Drude contribution (with an effective mass) to $\epsilon(\omega)$, and it has been long known that the Drude dielectric function

$$\epsilon_{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \tag{67}$$

[as distinct from the interband part of $\epsilon(\omega)$] *is* number conserving, i.e., (67) follows from (40) via (66); (b) since the onset for bulk-metal interband transitions ω_{IB} typically occurs in the visible or ultraviolet, the quantity $1/(\omega_{\text{IB}}\tau)$ is very small [0(1%) since for a metal $\tau \sim 10^{-14}$ sec].

In our case—the far-infrared behavior of small particles—there is no Drude term to swamp the discrete frequency contributions to ϵ, and $\omega\tau$ may be $O(1)$. Thus a number-conserving relaxation time approximation is important for obtaining meaningful numerical results. If the prescription for broadening (66) is applied to (47) we find

$$\text{Re}\,\epsilon(x) = 1 + \left[\frac{4}{\pi}\right]^4 \left[\frac{a}{a_0}\right] \sum_{m=1}^{m_c} m^2(m_c^2 - m^2) \sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2 - (x^2 + \Gamma^2)][1 - (-1)^{m+m'}]}{\Xi}$$

$$\text{Im}\,\epsilon(x) = \left[\frac{4}{\pi}\right]^4 \left[\frac{a}{a_0}\right] \frac{\Gamma}{x} \sum_{m=1}^{m_c} m^2(m_c^2 - m^2) \sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2 + (x^2 + \Gamma^2)][1 - (-1)^{m+m'}]}{\Xi} , \tag{68}$$

where

$$\begin{aligned} \Xi &= \Delta^3[(\Delta^2 - x^2 + \Gamma^2)^2 + 4x^2\Gamma^2] , \\ \Delta &= m'^2 - m^2 , \end{aligned} \tag{69}$$

and

$$x = \frac{\omega}{\omega_c} = \hbar\omega \Big/ \left[\frac{\hbar^2}{2m}\frac{\pi^2}{a^2}\right] .$$

Here $\Gamma = 1/\omega_c\tau = (\hbar/\tau)m_c^2/\varepsilon_F$ is the "linewidth"; we shall refer to (68) as the quantum size effect (QSE) result for $\epsilon(\omega)$.

IX. OPTICAL PROPERTIES

As a paradigm for the optical properties to be expected for small metallic particles, we will consider in detail the numerical results following from (68). Figure 1(a) shows the frequency-dependent optical conductivity [rather than $\epsilon(\omega)$, which becomes inconveniently large for low frequencies] for a cubic particle described by the bulk Drude parameters of Al but for $m_c = 32$. This corresponds to an equivalent volume sphere diameter of about 70 Å. We deliberately use the bulk Al τ since inclusion of surface scattering, via, for example, (13), is inappropriate when the presence of the surface directly determines the eigenstates within the particle volume.

The optical structure is readily interpreted via the selection rules; for general Δm odd, discrete absorption lines are expected to appear (for $m_c = 32$) at

$$x = \frac{\hbar\omega}{\varepsilon_F} = \frac{\Delta m}{m_c^2}[2m_c + \Delta m]$$

$$= 0.0635, 0.196, 0.337, \ldots . \qquad (70)$$

The amplitudes of the peaks decrease rapidly, roughly as $1/(\Delta m)^2$ in accordance with the matrix element (45). Furthermore, in Al and for $m_c = 32$ the linewidth $\Gamma \approx 7$, so that in the dimensionless representation (68) the discrete lines are expected to be strongly broadened; for smaller particles (for fixed τ) the lines would clearly be sharper.

The corresponding curves for a Drude metal of bulk Al are shown in Fig. 1(b) for comparison. Apart from the peak in Im σ at $\omega\tau = 1$ the only observation to be made is that the dc conductivity is a factor ~ 35 larger than for the QSE result of Fig. 1. Since we have emphasized that the infrared electric dipole absorption coefficient is *inversely* proportional to the dc conductivity, we conclude that quantum size effects will lead to far-infrared (FIR) absorption *larger* (with respect to the Drude prediction) by this factor.

As has been observed above, $\sigma(\omega)$ [or $\epsilon(\omega)$] is not *directly* measurable for a small particle. The optical properties of a dilute *suspension* of metallic particles, however, are directly accessible via *absorption* measurements. We thus display below results obtained by using (68) for $\epsilon(\omega)$ evaluated for *cubes* in the Maxwell-Garnett expression (7) appropriate for *spheres* in the usual expectation that the differences in optical behavior of a small sphere and a small cube are unimportant. For an

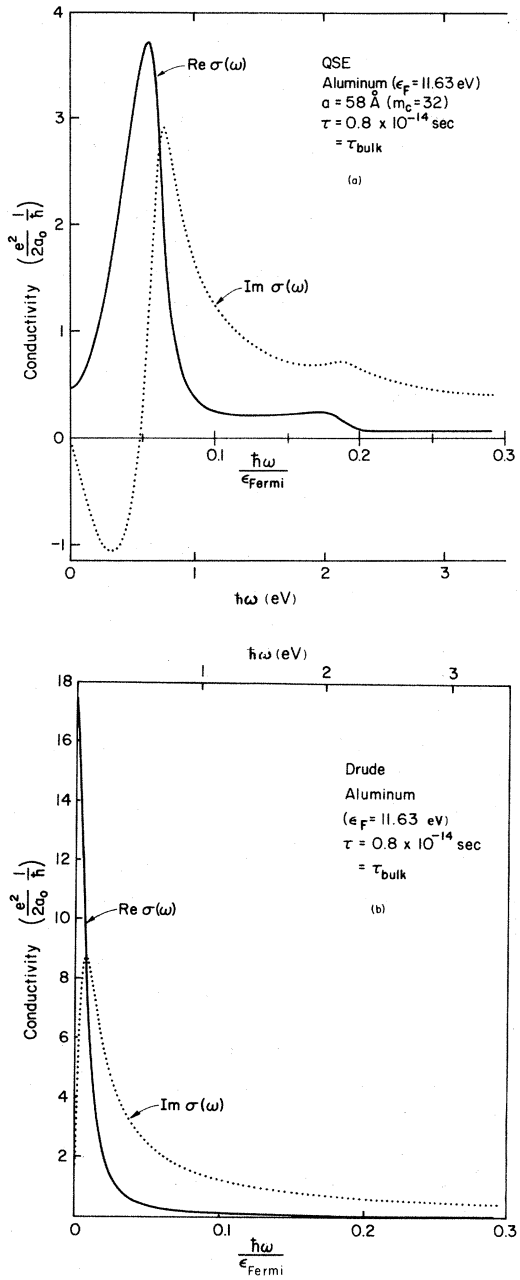

FIG. 1. (a) Frequency dependence of the optical conductivity of a small Al cube for bulk values of the Fermi energy and relaxation time. QSE denotes the quantum size effect result, Eq. (69). (b) Classical Drude model counterparts to the curves in (a).

Al sphere volume fraction η of 10% with bulk relaxation time τ, the absorption coefficient

$$\alpha(\omega)=\frac{2\omega}{c}\,\mathrm{Im}[\epsilon_{\mathrm{QSE}}(\omega)]^{1/2} \tag{71}$$

is shown in Fig. 2(a); very rapid oscillations on the high-frequency side of the sphere resonance have been suppressed for clarity. The classical bulk Drude result is shown for comparison. The extent to which the QSE absorption is enhanced in the FIR is evident; also prominent are the broadened discrete absorption peaks expected from (70) above. A "knee" marking the onset of the particle-in-a-box transitions at the threshold frequency

$$\frac{\hbar\omega_t}{\varepsilon_F}=(2m_c+1)/m_c^2 \tag{72}$$

(the most noticeable feature) occurs, however, at a frequency where $\alpha(\omega)$ is a factor $\sim 10^5$ smaller than its peak (sphere resonance) value.

In Fig. 2(b) is shown an enlargement (on a linear scale) of the behavior in the vicinity of the Mie sphere resonance, occurring in the Maxwell-Garnett approximation at

$$\left.\frac{\omega}{\omega_p}\right|_{\mathrm{sphere}}=\left[\frac{(1-\eta)}{3}\right]^{1/2}. \tag{73}$$

Even using the bulk relaxation time, the sphere resonance is considerably broadened using the $\epsilon(\omega)$ appropriate to the QSE. As mentioned in the context of the quasicontinuous limit above, the broadening occurs because of Landau damping of the collective surface plasmon excitation, which can decay into single-particle (particle-in-a-box) transitions.

X. THE METAL-INSULATOR TRANSITION

The m' sum in (47) above may be performed analytically (see the Appendix) and we may write down as a sum the dc conductivity of a single small cube; with the usual definition (59) we find

$$Q\equiv\frac{\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{QSE})}{\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{Drude})}=1-\frac{3+1/m_c}{4m_c}-\frac{48}{\Gamma^2 m_c^3\pi^2}\mathrm{Re}\sum_{m=1}^{m_c}m^2(m_c^2-m^2)\times\begin{cases}-z\tan z, & m\ \text{even}\\ +z\cot z, & m\ \text{odd}\end{cases} \tag{74}$$

where

$$z=\frac{\pi m}{2}\left[1-\frac{i\Gamma}{m^2}\right]^{1/2},$$

$$\mathrm{Re}\sigma_{\mathrm{dc}}(\mathrm{Drude})=\frac{\omega_p^2\tau}{4\pi}. \tag{75}$$

As the particle size grows Γ [Eq. (69)] grows also, so that roughly speaking, $\Delta^2+\Gamma^2\approx\Gamma^2$ in (68). As a consequence we may show from the f-sum rule that

$$\lim_{m_c\to\infty}\frac{\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{QSE})}{\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{Drude})}=1, \tag{76}$$

i.e., the dc tails of the broadened discrete peaks in $\mathrm{Re}\,\sigma(\omega)$ for a finite system merge as the particle grows larger and in such a way as to recover the dc Drude conductivity.

Though we have deliberately excluded the case $m_c\approx 1$ (i.e., particle dimensions $\sim 1/k_F$) as being beyond the regime of validity of the semiclassical treatment above, it should be remarked that for $m_c=1$, or $k_F a=\pi$, the small metallic cube ceases to be metallic since

$$\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{QSE},m_c=1)=0. \tag{77}$$

The condition $m_c=1$ corresponds, of course, to a very small particle. It is interesting to observe that the Ioffe-Regel criterion for localization of electrons in the presence of scattering,[47] i.e., breakdown of the Boltzmann equation approach to conduction in a solid, is

$$k_F L\lesssim 2\pi, \tag{78}$$

where L is the mean free path. If we crudely interpret L as a characteristic small-particle dimension, we are led to consider this cessation of conducting behavior as a metal-insulator transition of the Ioffe-Regel sort.

Thus in order to avoid the consequences of the $2k_F$ oscillations near the surface of a small particle

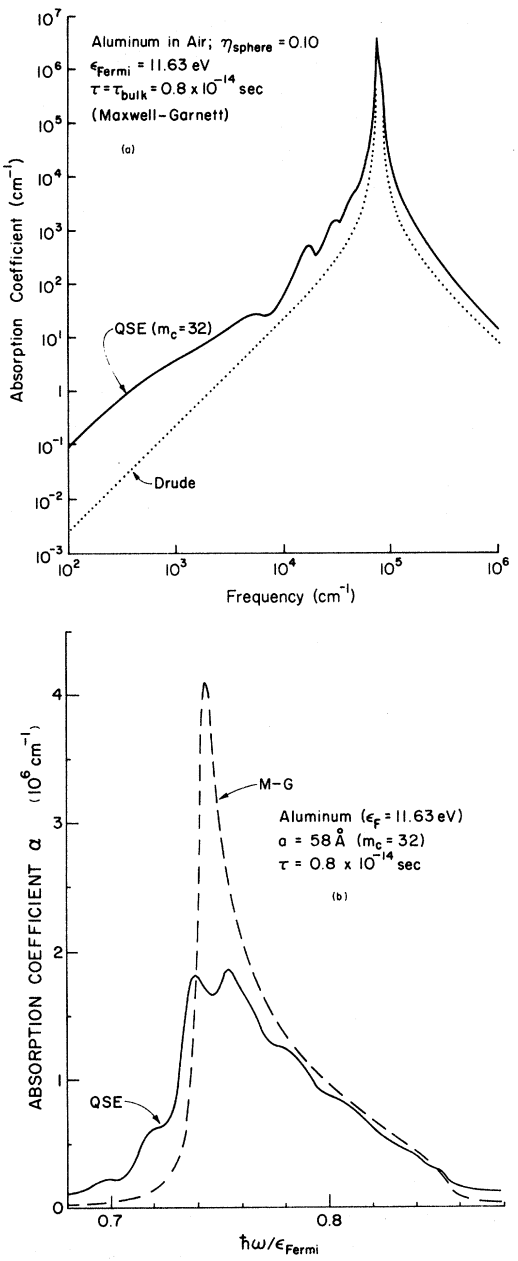

FIG. 2. (a) Frequency dependence of the absorption coefficient $\alpha(\omega)$ for a composite consisting of 10% volume fraction η of Al small particles in air, using the Maxwell-Garnett expression, Eq. (7) and the QSE $\varepsilon(\omega)$, Eq. (68). The classical Drude result is also shown. (b) Frequency dependence of the absorption coefficient in the vicinity of the Mie sphere resonance (linear scale).

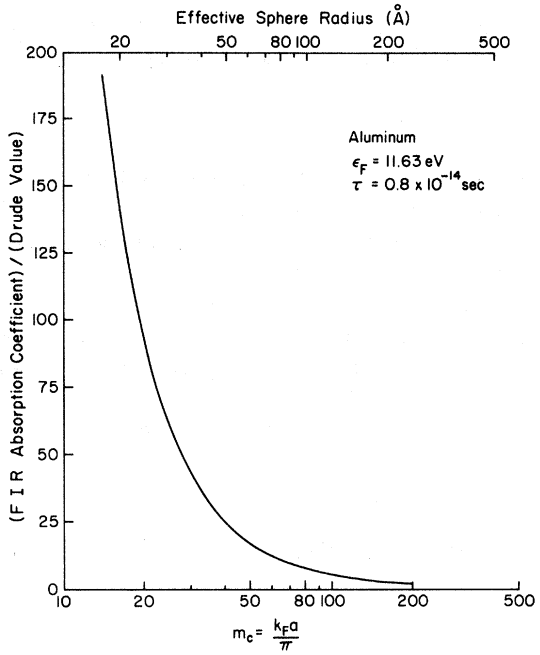

FIG. 3. Size dependence of the factor by which the QSE electric dipole absorption coefficient in the FIR exceeds the classical bulk (Drude) value.

we must choose $m_c \gg 1$: but this choice will also ensure that we avoid the metal-insulator transition as well. In this light the enhanced far-infrared electric dipole absorption coefficient for small particles is a natural consequence of the reduction in the dc conductivity as the small-particle dimension approaches the critical value at which the metal-insulator transition occurs. The ratio by which the FIR absorption coefficient is enhanced is simply $1/Q$ [see (14) and (74)], as shown for Al in Fig. 3. It would appear that for spheres of intermediate size, such as occur experimentally, the full magnitude of the FIR absorption cannot be accounted for by appeal to electric dipole quantum size effects *alone.* (See *Note added in proof.)*

XI. OBSERVATION OF QUANTUM SIZE EFFECTS

We have treated above the broadening of an individual peak in the discrete spectrum of a small particle in the presence of scattering. There remains the question of whether the discrete structure itself will be experimentally detectable. We may establish a possible criterion by observing that all of the prominent discrete transitions occur for frequencies of order the gap

$$\omega_t = \frac{\varepsilon_F}{\hbar}\frac{(2m_c+1)}{m_c^2} \underset{(m_c\to\infty)}{\to} \frac{\pi v_F}{a} . \tag{79}$$

If there is some characteristic relaxation time τ in the electronic system (due to phonon scattering or

impurities, for example) we require

$$\frac{\pi v_F}{a} >> \frac{1}{\tau} \tag{80}$$

in order that the discrete spectrum manifest itself. This criterion is precisely that the semiclassical surface-scattering rate considerably exceed the bulk scattering rate in (13). Inverting the logic, if (80) is obeyed, the whole scheme for slightly modifying the Drude model via (13) breaks down, and a treatment such as the QSE approach above is required.[48]

In this picture we do not expect temperature to play a significant role in destroying the optical structure of an ultrafine metal particle. Temperature effects presumably set in when, for large m_c

$$\hbar\omega_t \cong \frac{2}{m_c}\varepsilon_F \sim k_B T \tag{81}$$

or

$$\frac{\bar{R}}{a_0} \sim \frac{\varepsilon_F}{(k_B T)(k_F a_0)} \tag{82}$$

in terms of an equivalent volume sphere radius. For Al at 300 K this critical $\bar{R}$ is about 1000 Å, by which point the damping factor Γ for the discrete levels is so large that no optical structure would in any event be observable.[49]

Small particles are commonly produced by condensation and coalescence of the metal in question in the vapor phase; often a good representation of the resulting particle size distribution is the "log normal" form:

$$P(r) = \frac{1}{r}\frac{1}{\sqrt{2\pi}}\frac{1}{\ln\sigma}\exp\left[-\left[\frac{\ln r/\bar{r}}{\sqrt{2}\ln\sigma}\right]^2\right], \tag{83}$$

where $P(r)dr$ is the probability of finding a particle of radius between r and $r+dr$. Typically $\bar{r}$ may be 30 Å and $\sigma \approx 1.4$ for an experimental sample. Because the logarithm of the particle size is distributed normally, the distribution is in principle rather broad, and we expect most details of the discrete optical structure to be smeared out unless σ can be made close to unity. In any case an enhanced far-infrared absorption coefficient will persist, and the "knee" corresponding to absorption at the "gap" [see Fig. 3(a)] may remain visible.

In the vicinity of the sphere resonance, however, one continues to expect the broadening due to Landau damping discussed earlier. A distribution of particle sizes will probably further broaden this feature insofar as the position of the surface plasmon itself is expected to depend weakly on particle size. We may use (49) to estimate crudely this size dependence, assuming the sphere resonance occurs at high frequencies; we find

$$\left.\frac{\omega^{\mathrm{QSE}}}{\omega_{\mathrm{class}}}\right|_{\mathrm{spheres}} = \left[1 - \frac{3}{4m_c} - \frac{1}{4m_c^2}\right]^{1/2} . \tag{84}$$

Although this result should be regarded as approximate only (it follows from an expression which weakly violates the f-sum rule), it does reflect the anticipated reduced ability of a bounded electron gas to screen the externally applied field. For $m_c = 1$, where the metal-insulator transition occurs, there is no sphere resonance in this simple treatment. When m_c has reached 10, however, the QSE result has attained 96% of the bulk Drude resonance frequency, justifying our assumption that the Mie resonance remains a high-frequency feature even for very small metal particles. The prediction of a shift to frequencies lower than bulk values is in qualitative agreement with some experimental results.[50]

XII. MULTIPOLE EFFECTS

It may be expected on the basis of the classical treatment of optical absorption above that quantum multipole effects might also be important. A quantum multipole expansion, like its classical counterpart, will take the form of an expansion in powers of qa, where a is the characteristic small dimension of the system. However, the general $q \neq 0$ electrodynamics of response to the self-consistent field is fraught with difficulties because the local field may no longer be taken as purely transverse.

For an atomic system this question almost never arises, and $\vec{A}$ is taken to be the vector potential of the incident (transverse) light wave. Under these assumptions, (36) becomes

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{8\pi e^2}{\Omega m^2 \omega^2}\sum_{ij}\frac{f_i \varepsilon_{ij} \left| \langle i | e^{i\vec{q}\cdot\vec{r}} \hat{p}_E | j \rangle \right|^2}{(\varepsilon_{ij}^2 - \hbar^2\omega^2)} . \tag{85}$$

Expanding the exponential one first recovers the electric dipole term (for $q = 0$) and then, to next order in q, the electric quadrupole and magnetic dipole terms.[51]

The use of cubical box wave functions ceases to be convenient when $q \neq 0$ because the square modulus of the matrix elements above fails to decouple into pure multipole pieces. We may estimate the effect of the magnetic dipole term in a semiclassical way. Just as the fundamental quantity in the Mie expansion is the dielectric function $\epsilon(\omega)$, which enters in the specification of *both* electric and magnetic multipoles, we might expect that the electric dipole RPA result for $\epsilon(\omega)$, when substituted into the *classical* expression for the magnetic dipole term, may mimic the full quantum magnetic dipole contribution. Since we have discovered that the dc electric dipole conductivity of a small particle is suppressed by a factor $O(10-100)$, Eq. (14) above suggests that quantum size effects will merely push to larger particle sizes the point at which magnetic dipole absorption will dominate dipole absorption.

The significant conclusions from the work described above are not restricted to the particle-in-a-box model. We observe that: (i) for comparison between theory and experiment it is important to introduce electron lifetime effects rather carefully; (ii) an enhanced FIR electric dipole absorption coefficient for metal microparticles is a simple harbinger of the metal-insulator transition generally believed to occur for sizes $L \sim 1/k_F$; (iii) some of the width of the Mie sphere resonance is due to Landau damping, itself a quantum size effect; and (iv) it seems unlikely electric dipole or semiclassical multipole contributions can account for the small particle FIR absorption anomaly.

Two points in particular deserve further scrutiny. First, no rigorous justification for the use of a Kubo gap $\sim \varepsilon_F/N$ (as opposed to the geometrical high-symmetry gap $\sim \varepsilon_F/N^{1/3}$ used here) has yet been given for small particles. Second, the role of quantum multipoles higher than the electric dipole case considered here should be assessed with a view to explaining the experimental excess far-infrared absorption.

Note added in proof. We point out that a divergence of the level spacing at the Fermi level $\Delta(k_F)$ (an alternative indication of a metal-insulator transition) for particles sized $\sim 1/k_F$ follows generally from the use of Dirichlet boundary conditions for free electrons in a container of reasonable shape. An expression for the average mode density [H. Baltes and E. Hilf, *Spectra of Finite Systems* (Bibliographisches Institut, Mannheim, 1976), Secs. V.3 and VI.2] for a cube of side L may be used to extract $\Delta(k_F)$:

$$\Delta(\epsilon_F) = 1 \Big/ \left[\frac{d\bar{N}}{dE} \right]_{k_F}$$

$$= \tfrac{1}{2}\epsilon_F / [\tfrac{1}{4}\pi x^3 - \tfrac{3}{8}\pi x^2 + \tfrac{3}{8}x + \cdots]$$

for $x = k_F L/\pi$. Formally valid for large x, it has been found numerically to represent well the average level spacing even for $x \gtrsim 1$. The terms in brackets correspond to volume, surface, edge, vertex, etc., contributions. For $x \to \infty$ one recovers the bulk value $\frac{2}{3}\,\epsilon_F/N$; at $x = 1.04$ (or $k_F\bar{R}/\pi = 0.646$) $\Delta(k_F)$ diverges. This is very close to the value $m_c = k_F a/\pi = 1$ found in the text for "cubes"; a similar calculation for $\Delta(k_F)$ for spheres yields $k_F R/\pi = 0.572$ where Δ diverges.

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APPENDIX

In the absence of dissipation (i.e., $\tau = \infty$) Eq. (36) of the text is, using the matrix element (45),

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} + \left[\frac{4}{\pi}\right]^5 \frac{(a/a_0)}{x^2} \left[\frac{a^3}{\Omega}\right] \sum_{m,n,p \geq 1}^{\infty} m^2 f_{mnp} \sum_{m'=1}^{\infty} \frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)[(m'^2-m^2)^2-x^2]}\,, \tag{A1}$$

where $x = (\hbar\omega)/[(\hbar^2/2m)(\pi^2/a^2)]$ and f_{mnp} is the Fermi occupation factor for the state (m,n,p). The m' sum may be written

$$\sum_{m'=1}^{\infty} \frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)[(m'^2-m^2)^2-x^2]} = -\frac{1}{2x}[S(m,x)-S(m,-x)] , \tag{A2}$$

where

$$S(m,x)=\sum_{m'=1}^{\infty} \frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)(m'^2-m^2+x)} . \tag{A3}$$

Now S is a function only of $|m'|$ since $(-1)^{-m'}=(-1)^{m'}$, so, writing $m'^2=(m'^2-m^2)+m^2$ in the numerator of S and letting $(m'-m)\equiv p$,

$$S(m,x)=\frac{1}{2}\left[\sum_{p=-\infty}^{\infty} \frac{[1-(-1)^p]}{[p(p+2m)+x]} + m^2 \sum_{p=-\infty}^{\infty} \frac{[1-(-1)^p]}{p(p+2m)[p(p+2m)+x]}\right] . \tag{A4}$$

Here p must be odd to contribute, so letting $p=2k+1$,

$$S=\sum_{k=-\infty}^{\infty} \frac{1}{[(2k+1)(2k+2m+1)+x]} + m^2 \sum_{k=-\infty}^{\infty} \frac{1}{[(2k+1)(2k+1+2m)]} \frac{1}{[(2k+1)(2k+1+2m+x)]} . \tag{A5}$$

Now we use the familiar theorem from complex analysis[52] that for a well-enough behaved function $F(x)$

$$\sum_{n=-\infty}^{\infty} F(n) = -\pi \sum_{k=1}^{m} \mathrm{Res}[F(z)\cot \pi z]_{z=a_k} , \tag{A6}$$

where the $\{a_k\}_{k=1,m}$ are the poles of F. The F's above are quite simple. After some effort we find

$$S(m,x)=\frac{\pi}{4}\left[\frac{m^2-x}{x}\right]^{1/2} (\cot \pi z_1 - \cot \pi z_2) , \tag{A7}$$

where

$$z_1=\frac{-(1+m)+(m^2-x)^{1/2}}{2}, \quad z_2=\frac{-(1+m)-(m^2-x)^{1/2}}{2} . \tag{A8}$$

Hence

$$S(m,x)-S(m,-x)=\begin{cases} -\dfrac{1}{x}(u\tan u + v\tan v) & (m \text{ even}) \\ +\dfrac{1}{x}(u\cot u + v\cot v) & (m \text{ odd}) \end{cases} , \tag{A9}$$

where

$$u=\frac{\pi}{2}(m^2+x)^{1/2}, \quad v=\frac{\pi}{2}(m^2-x)^{1/2} . \tag{A10}$$

Static dielectric constant

We may perform an expansion in small x of $S(m,x)-S(m,-x)$ to find, after much labor, for m odd or even

$$-\frac{1}{2x}[S(m,x)-S(m,-x)] = \frac{\pi^2}{32m^2} - \frac{x^2\pi^2}{1536m^4}\left[\pi^2 - \frac{15}{m^2}\right] + O(x^4) . \tag{A11}$$

We may also expand out directly the m' sum for small x, identifying

$$\sum_{m'=1}^{\infty} \frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)^3} = \frac{\pi^2}{32m^2} \tag{A12}$$

and

$$\sum_{m'=1}^{\infty} \frac{m'^2[1-(-1)^{m+m'}]}{(m'^2-m^2)^5} = \left[\frac{15}{m^2}-\pi^2\right]\frac{\pi^2}{1536m^4} . \tag{A13}$$

In the text it is demonstrated in general that $m/m^*=0$ for a genuinely discrete system. Hence as $\omega \to 0$, using the substitution (46) in (A1)

$$\lim_{\omega\to 0}\epsilon(\omega)=\epsilon_0=1+\left[\frac{4}{\pi}\right]^4\left[\frac{a}{a_0}\right]\frac{\pi^2}{1536}\left[15m_c^2\left[S_4-\frac{S_2}{m_c^2}\right]+\pi^2 m_c(1-m_c S_2)\right], \tag{A14}$$

where

$$S_2=\sum_{m=1}^{m_c}\frac{1}{m^2},\quad S_4=\sum_{m=1}^{m_c}\frac{1}{m^4} \tag{A15}$$

which is Eq. (50) of the text.

For large m_c the sums S_2 and S_4 are readily expanded out[53]:

$$\begin{aligned}S_2&=\frac{\pi^2}{6}-\frac{1}{m_c}+\frac{1}{2m_c^2}-\frac{1}{6m_c^3}+\cdots,\\ S_4&=\frac{\pi^4}{90}-\frac{1}{3m_c^3}+\frac{1}{2m_c^4}-\frac{1}{3m_c^5}.\end{aligned} \tag{A16}$$

For large m_c we find, with $m_c=k_F a/\pi$,

$$\lim_{m_c\to\infty}\epsilon_0=1+\frac{k_F a_0}{3\pi}\left[\frac{a}{a_0}\right]^2, \tag{A17}$$

which is Eq. (51) of the text.

Static conductivity

While it may be easily shown that

$$\begin{aligned}\mathrm{Re}\,\sigma(\omega=0)&=\lim_{\omega\to 0}\frac{\omega}{4\pi}\,\mathrm{Im}\,\epsilon(\omega)\\ &=\frac{1}{4\pi\tau}\left[\mathrm{Re}\,\epsilon\left[\omega=\frac{i}{\tau}\right]-1\right],\end{aligned} \tag{A18}$$

we will use (68) directly. Using the units defined there we find that

$$\begin{aligned}Q&=\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{QSE})/\mathrm{Re}\,\sigma_{\mathrm{dc}}(\mathrm{Drude})\\ &=\frac{48\Gamma^2}{\pi^2 m_c^3}\sum_{m=1}^{m_c}m^2(m_c^2-m^2)\\ &\quad\times\sum_{m'=1}^{\infty}\frac{m'^2[1-(-1)^{m+m'}]}{\Delta^3(\Delta^2+\Gamma^2)}.\end{aligned} \tag{A19}$$

Now

$$\frac{1}{\Delta^3(\Delta^2+\Gamma^2)}=\frac{1}{\Gamma^2}\left[\frac{1}{\Delta^3}-\frac{1}{\Delta(\Delta^2+\Gamma^2)}\right], \tag{A20}$$

and we may use (A12) to evaluate the $1/\Delta^3$ piece. The final term is of the form (A2) with $x=i\Gamma$. Hence

$$\begin{aligned}Q&=1-\frac{(3+1/m_c)}{4m_c}\\ &\quad-\frac{48}{\Gamma^2\pi^2 m_c^3}\mathrm{Re}\sum_{m=1}^{m_c}m^2(m_c^2-m^2)\\ &\quad\times\begin{cases}-z\tan z, & m\ \text{even}\\ +z\cot z, & m\ \text{odd}\end{cases}\end{aligned} \tag{A21}$$

$$z=\frac{\pi m}{2}(1-i\Gamma/m^2)^{1/2}. \tag{A22}$$

This form for Q explicitly vanishes when $m_c=1$. The finite sum[54]

$$\sum_{k=1}^{n}k^2=\frac{n(n+1)(2n+1)}{6} \tag{A23}$$

is also useful in evaluating the effective mass and the $\epsilon(\omega\to\infty)$ limit.

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