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Electric dipole absorption by ballistic electrons in small metal spheres

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Abstract. We describe a semiclassical approach to estimating the absorption of electromagnetic radiation by small conducting spheres, in which the motion of the charge carriers is ballistic. The results are strikingly different between the cases of rough and smooth walled particles. For a rough walled particle the absorption coefficient is proportional to ω^2 in the low-frequency limit. For a smooth walled sphere the absorption coefficient has a low-frequency cut-off at ω_c, the angular frequency of a circumferential 'whispering gallery' classical orbit of a carrier at the Fermi surface. At frequencies above ω_c the spectrum consists of a sequence of overlapping resonance bands which combine to give an absorption coefficient proportional to ω^2 only for $\omega \gg \omega_c$.

1. Introduction, review and principal results

1.1. Introduction

The absorption of radiation by small metallic particles is a subject of considerable interest; experimental and theoretical work in this field has recently been reviewed by Perenboom *et al* [1], Carr *et al* [2] and Halperin [3]. In this paper we analyse the case where the motion of the charge carriers is ballistic (i.e. where the mean free path is much larger than the dimensions of the particle); this has not previously received a fully satisfactory treatment. We model the charge carriers (which we will refer to as electrons) by a gas of non-interacting fermions characterized by a charge e and isotropic effective mass m. The potential energy is taken to be uniform inside the boundary of the small metal particle, and infinite outside. We give an analysis of this system based on the semiclassical approach [4], in which the dynamics of the electrons is modelled by classical trajectories, and the eigenfunctions and energy levels are not required. We consider only spherical particles: it will become apparent that a theory for arbitrary shapes would not be tractable. Our objective is to give physical insights into the problem using this simplified model, and to give some explicit results that could be used as a benchmark against which fully quantum mechanical calculations could be compared.

We begin by describing the various types of electron dynamics and frequency regime for this problem. If the size of the conducting particles is large compared to the Fermi wavelength, it is meaningful to consider the classical motion of the electrons, which may be classified as either diffusive or ballistic. In the diffusive regime an electron is scattered many times as it traverses a distance equal to the particle radius a, and can be characterized by a bulk conductivity. In very small particles the motion is ballistic, i.e. the electron bounces off the walls of the particle many times between internal scattering events. The

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case of diffusive electron motion is adequately treated in the early classical work of Mie [5] on absorption and scattering by dielectric spheres. In this paper we only consider ballistic electron motion.

If the electron motion is ballistic, it is useful to distinguish between chaotic and integrable classical motion of the electrons (the relevant concepts are reviewed by Gutzwiller [6]). If the particle has a smooth surface, so that the electrons are reflected specularly at the boundary, integrable classical motion will occur for some shapes of the boundary. In particular, motion of electrons in a smooth walled spherical enclosure is integrable, because angular momentum is conserved. However, some other smooth boundaries are known to give chaotic classical motion [7]. If the boundary of the particles is rough, or the internal scattering is significant, the electron dynamics is chaotic. The specular reflections required for integrable motion can be realized physically if the effective surface roughness of the boundary is small compared to the Fermi wavelength. The Fermi wavelength can be very large compared to the atomic scale in systems (such as semiconductors or bismuth) with very low densities of charge carriers. Our calculations will show a marked difference between the absorption spectra of rough and smooth walled particles, which is characteristic of the different types of classical electron dynamics.

Our model for the small metal particle has three characteristic frequency scales. The lowest characteristic frequency, which we denote by ω_0, is associated with the typical spacing ΔE of the single-particle energy levels: $\omega_0 = \Delta E/\hbar$. The highest characteristic frequency is the plasma frequency ω_p: below ω_p the electron gas is able to screen out the applied electric field from the interior of the particle, whereas above ω_p there is a uniform internal electric field. Intermediate between these two frequencies is a third frequency ω_c, which is the typical frequency of collisions of an electron with the surface of the particle: $\omega_c = v_F/a$, where v_F is the Fermi velocity. In this paper we will be primarily interested in what happens above the level spacing freqency ω_0 but below the plasma frequency ω_p. We pay less attention to the response above the plasma frequency, because the applicability of semiclassical methods is somewhat limited in this regime. Analysis of the response at or below ω_0 requires a fully quantum approach, and is outside the range of this paper.

1.2. Brief review of relevant literature

There is a large theoretical literature on the interaction of small metal particles with electromagnetic radiation. To establish connections with the present work, we briefly review some of the principal contributions.

(a) Classical electromagnetic calculations of the absorption and scattering of radiation by dielectric spheres were carried out by Mie [5] and Garnett [8,9]. The Mie theory is appropriate for the case of diffusive electron dynamics, where the dielectric constant is characterized by a bulk conductivity. The extension to ballistic dynamics is unclear, although many authors have used an effective conductivity derived by replacing the relaxation time τ in the Drude model [4] with a time a/v_F characterizing the frequency of collisions with the walls. We will term this the effective conductivity *ansatz*.

(b) Kawabata and Kubo [10] have calculated the absorption coefficient quantum mechanically for the case of ballistic electron motion, at frequencies above the plasma frequency. These results have been extended [11] and corrected [12] by others. The calculation depends on a knowledge of the electron wavefunctions, and for this reason it can only be carried through for a smooth walled sphere and some other geometries with classically integrable dynamics.

(c) Gorkov and Eliashberg [13] studied the structure of the absorption coefficient in the vicinity of ω_0 using random matrix theory. Their calculation contains a significant error in

that it ignores screening of the external electric field due to surface charges [14]; an algebraic error has also been corrected [15]. Gorkov and Eliashberg assume that the single-particle energy levels have random matrix spectral statistics. More recent work on semiclassical quantum mechanics, reviewed by Gutzwiller [6], indicates that this assumption is valid for a rough walled particle, in which the electron motion is chaotic, but not for a smooth walled spherical particle in which the electron dynamics is integrable.

(d) A large number of quantum mechanical calculations employing self-consistent field methods have been described; some examples are [16]–[18], and references therein. These studies have concentrated on exactly spherical geometries, and do not discuss the distinction between the behaviour of rough and smooth walled particles.

(e) There is a close analogy between the dynamics of electrons in small metal particles and the motion of nucleons in the collective model of the nucleus. Various workers [19,20] have discussed semiclassical models for dissipation in nuclear processes that are analogous to the approach we adopt here. The principal difference is that the perturbation is a displacement of the nuclear surface rather than an externally applied field.

1.3. Principal results

The organization of this paper and its principal results are as follows.

(a) In section 2 we give a semiclassical discussion of the absorption of energy by an electron gas due to an external perturbation. The principal result, equation (2.6), should be very widely applicable in semiclassical analyses of absorption of energy by electrons in ballistic systems.

(b) Section 3 discusses the effect of an externally applied electric field, with a frequency below the plasma frequency, on the energy of electrons rebounding from the wall of the particle. Our analysis, based on a Thomas–Fermi approach, appears to be the first treatment of the effect of screening of the applied electric field on the dynamics of the electrons.

(c) In section 4 we consider the case of ballistic electrons confined to a smooth walled sphere. We find that the absorption coefficient vanishes below a cut-off $\omega_c = v_F/a$, which we will term the 'bounce frequency'. Above ω_c, the absorption spectrum contains an increasing number of overlapping bands, which sum to a quadratic frequency dependence in the limit $\omega \gg \omega_c$. The coefficient of this quadratic dependence differs from that obtained from the effective conductivity *ansatz* by a material dependent parameter. In the neighbourhood of the bounce frequency, the frequency dependence of the absorption spectrum has a complex structure reminiscent of that predicted by Gorkov and Eliashberg. Both phenomena are related to the crossover between a discrete and a quasi-continuous spectrum, but beyond that they are unrelated: our result concerns the smooth walled sphere close to ω_c, whereas theirs refers to a rough walled system close to ω_0.

(d) Ballistic electrons confined to a rough walled sphere are discussed in section 5. We describe a realistic model for the rough walled sphere, in which the absorption coefficient is proportional to ω^2 both above and below the bounce frequency ω_c. The distinction between the rough and the smooth surface illustrates an earlier analysis by one of us [21] which predicts that at low frequencies the rate of dissipation should be greatly suppressed in systems with integrable dynamics. We also describe a novel mechanism by which the absorption of energy is enhanced by the roughness of the surface.

(e) In section 6 we present, for completeness, a semiclassical analysis of the absorption of radiation above the plasma frequency, giving results in agreement with those of the Kawabata and Kubo method where they overlap. Our theory only applies if $\hbar\omega_p$ is small compared to the Fermi energy E_F, but it is applicable to arbitrary geometries.

Our results are confined to considering electric dipole absorption. At frequencies below the plasma frequency, magnetic dipole absorption may be the dominant process in sufficiently large particles with diffusive electron dynamics, because the electric field is screened from the interior of the particle. We hope to publish a corresponding semiclassical analysis of magnetic dipole absorption with ballistic electron motion at a later date.

2. Semiclassical model for energy absorption

We characterize the electron gas by its phase space density $f(\boldsymbol{r}, \boldsymbol{p}, t)$, representing the number of electrons per unit volume in the single-particle phase space at coordinates $\boldsymbol{r} = (x, y, z)$ and momenta $\boldsymbol{p} = (p_x, p_y, p_z)$ at time t. To simplify the notation we will abbreviate the set of phase space coordinates by a single symbol α, and write the phase space density as $f(\alpha, t)$. Because the electrons are regarded as independent quasiparticles, their dynamics is defined by a single-particle Hamiltonian $H(\boldsymbol{r}, \boldsymbol{p}, t) = H(\alpha, t)$. This consists of an unperturbed part plus a sinusoidally oscillating term proportional to the applied electric field $\mathcal{E}$:

$$H(\alpha, t) = H_0(\alpha) + \mathcal{E}_0 H_1(\alpha) \sin \omega t. \tag{2.1}$$

It will also be useful to consider a coordinate system in phase space where the position α is labelled by the unperturbed energy $E = H_0(\alpha)$ and a set of five other coordinates Σ, describing the position on the energy shell at energy E, which we need not specify in detail. We will write $\mathrm{d}\alpha = \mathrm{d}E\, \mathrm{d}\Sigma(E)$ for the volume element in phase space.

We assume that the system is initially in its ground state, for which the phase space density corresponds to the zero-temperature Fermi–Dirac distribution:

$$f(\alpha, 0) = 2h^{-3}\Theta[E_\mathrm{F} - H_0(\alpha)] \tag{2.2}$$

where E_F is the Fermi energy and $\Theta(x)$ is the unit increasing step function. A factor of two is included in (2.2) to account for spin degeneracy. After applying the perturbation for a time t, the phase space coordinates of an electron initially at α are transformed to α_t, and the energy of each electron will have changed by a small amount $\Delta E(\alpha, t)$ which will be computed by using classical perturbation theory (see figure 1). We must consider how to compute the change in the total energy of the electron gas from the change in the energies of the individual particles, ΔE.

The total energy E_T of the electron gas is the sum of the single-particle energies. Approximating this sum by an integral, this is

$$\begin{aligned} E_\mathrm{T}(t) &= \int \mathrm{d}\alpha\, f(\alpha, t) H_0(\alpha) = 2h^{-3} \int \mathrm{d}\alpha\, \Theta[E_\mathrm{F} + \Delta E(\alpha) - H_0(\alpha)]\, H_0(\alpha) \\ &= 2h^{-3} \int \mathrm{d}E \int \mathrm{d}\Sigma(E)\, E\, \Theta[E_\mathrm{F} + \Delta E(\Sigma, E) - E]. \end{aligned} \tag{2.3}$$

Now we subtract the initial total energy $E_\mathrm{T}(0)$ to find the total energy absorbed. We can replace the measure of the energy surface $\mathrm{d}\Sigma(E)$ in the integral over Σ by $\mathrm{d}\Sigma(E_\mathrm{F})$ because the integrand of the energy integral is zero except for a small interval of width $\sim \Delta E$ close to E_F:

$$\begin{aligned} \Delta E_\mathrm{T}(t) = E_\mathrm{T}(t) - E_\mathrm{T}(0) &= 2h^{-3} \int \mathrm{d}\Sigma(E_\mathrm{F}) \int \mathrm{d}E\, E\, [\Theta(E_\mathrm{F} + \Delta E - E) - \Theta(E_\mathrm{F} - E)] \\ &= 2h^{-3} \int \mathrm{d}\Sigma(E_\mathrm{F})\, [E_\mathrm{F} \Delta E(\Sigma) + \tfrac{1}{2} \Delta E^2(\Sigma)]. \end{aligned} \tag{2.4}$$

The volume V of the phase space enclosed by any surface is constant, i.e.

$$\delta V = 0 = \int d\alpha\,[f(\alpha,t) - f(\alpha,0)] \tag{2.5}$$

$$= \int d\Sigma(E_F) \int dE\,[\Theta(E_F + \Delta E - E) - \Theta(E_F - E)] = \int d\Sigma(E_F)\,\Delta E(\Sigma).$$

Comparison with (2.5) shows that the component of (2.4) that is linear in ΔE vanishes, and that the energy absorbed is therefore

$$\Delta E_T(t) = h^{-3} \int d\Sigma(E_F)\,\Delta E^2(\Sigma, E_F) = h^{-3}\Omega(E_F)\langle\Delta E^2(E_F)\rangle \tag{2.6}$$

where $\langle\Delta E^2(E_F)\rangle$ is the variance of ΔE for electrons initially at the Fermi energy, and $\Omega(E)$ is the weight of the energy shell at energy E:

$$\Omega(E) = \int d\Sigma(E) = \int d\alpha\,\delta[E - H_0(\alpha)]. \tag{2.7}$$

In all of the calculations below we find that the energy absorbed grows linearly with time, apart from unimportant fluctuations that oscillate with the frequency ω of the applied field. For this reason it is possible to characterize dE_T/dt by its cycle averaged value.

Equation (2.6) has been given in an earlier paper [21], where it was derived under the assumption that the energies of individual electrons evolve diffusively. The more general derivation above is included because, although this assumption is valid for low-frequency perturbations of electrons undergoing chaotic motion [22], it does not hold for electrons undergoing integrable motion.

The quantity $h^{-3}\Omega(E_F)$ is the density of states at E_F multiplied by the volume of the particle; as this expression is required for the calculations described later, we quote it here for a spherical particle of radius a:

$$h^{-3}\Omega(E_F) = a^3 m k_F / 3\hbar^2\pi \tag{2.8}$$

where k_F is the Fermi wavevector.

The quantity most frequently used to characterize the rate of absorption is the absorption coefficient γ, which is the fractional loss of the energy density of the incident radiation per unit distance along the path of the beam, and this is conventionally expressed as a function of the volume fraction $\mathcal{F}$ of the particles. Using the fact that the energy density of the electromagnetic field is $\frac{1}{2}\epsilon_0\mathcal{E}_0^2$, we find

$$\gamma = \frac{3\mathcal{F}}{4\pi a^3 \epsilon_0 c} \frac{1}{\mathcal{E}_0^2} \left\langle \frac{dE_T}{dt} \right\rangle \tag{2.9}$$

where $\langle dE_T/dt\rangle$ is the time averaged rate of absorption of energy for a single metallic particle.

3. Interaction of electrons with the particle boundary

3.1. Surface charges and screening

In this section we discuss the interaction of the electrons with the external electric field. Although we model the electron gas by a system of independent particles described by a single-particle Hamiltonian, the potential energy experienced by a single electron depends on the phase space distribution of the other electrons. The plasma frequency

$$\omega_p = [n(E_F)e^2/\epsilon_0 m]^{1/2} \tag{3.1}$$

where $n(E_F)$ is the number of electrons per unit volume at the Fermi energy and m is the effective mass, separates two regimes in the response of the electron gas. Below ω_p, the electron gas is able to rearrange itself in order to screen out the applied electric field from the bulk of the particle, by developing a surface charge. At frequencies above ω_p the electron gas is not able to respond quickly enough to create significant screening, and there is a uniform internal electric field, which for simplicity we will assume is identical to the applied external field $\mathcal{E}$. (The polarization of the background lattice may have an even higher cut-off frequency: this can be taken account of by reducing the internal field by an appropriate factor.)

We do not discuss the behaviour of the system at frequencies close to the plasma frequency, as this appears to be very difficult. Instead we describe two distinct models for calculating the change in the electron energies below and above ω_p. In both cases we find that the energy of the electrons changes discontinuously when they collide with the boundary of the particle. In this section we calculate the change δE of the energy of an electron due to a single collision with the boundary when $\omega \ll \omega_p$. Discussion of the case $\omega \gg \omega_p$ is deferred until section 6.

We discuss the low-frequency behaviour using a Thomas–Fermi analysis, in which the electrons move in a classical self-consistent field that incorporates the potential due to the other electrons as well as the background potential. The applied electric field $\mathcal{E}$ causes a small change δV in the potential experienced by an electron which causes a corresponding change δn in the electron density [4]:

$$\delta n = (3n/2E_F)\delta V \tag{3.2}$$

provided that $\omega \ll \omega_p$. The perturbation is screened out over a length scale λ_s comparable to the Fermi wavelength λ_F.

The effect of the external field is to induce a surface charge q per unit area, which is related to the potential δV as follows:

$$q = e\int \mathrm{d}z\, \delta n(z) = \frac{3en}{2E_F}\int \mathrm{d}z\, \delta V(z) \tag{3.3}$$

where z is a coordinate that measures distance normal to the surface of the particle. Classical electrostatics shows that for a sphere this surface charge at a given point is [23]

$$q = 3\epsilon_0 \mathcal{E}\cos\chi \tag{3.4}$$

where χ is the polar angle of the point relative to the direction of the field. Figure 2 illustrates the interpretation of the angle χ. Comparison with (3.3) enables the integral of $\delta V(z)$ to be evaluated.

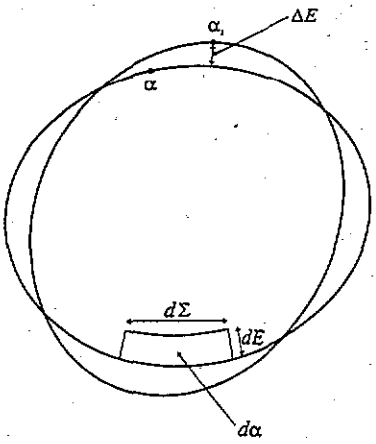

Figure 1. Schematic illustration of the region of phase space filled by the electron gas before and after applying a perturbation: a phase space point α with energy $H_0(\alpha) = E_F$ is mapped to a point α_t with energy $E_F + \Delta E(\alpha, t)$.

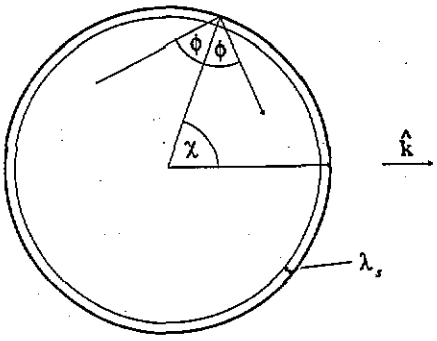

Figure 2. At low frequencies, the surface charge is confined to a narrow layer of width λ_s. The angle of reflection and the polar angle of the point of impact of an electron trajectory are ϕ and χ respectively (these angles need not lie in the same plane).

3.2. Effect of surface potential on electron energies

Now we consider the effect of the potential $\delta V(z)$ on the motion of the electrons. If the electric field is changing while an electron bounces off the boundary of the particle, the energy of the rebounding electron will change by an amount δE. We now calculate the change in energy of the electron as it collides with the boundary of the particle and encounters the potential $\delta V(z)$ induced by the external field. For simplicity we consider a simplified model in which the electrons are confined in the volume bounded by two flat parallel planes with separation L. The potential therefore only depends on one coordinate z, so that the analysis is essentially one dimensional.

The time dependent electric field $\mathcal{E}(t)$ gives rise to a varying potential $\delta V(z)\cos\omega t$ in the vicinity of the surface. In order to evaluate the effect of this time dependent perturbation, we expand the wavefunction as follows:

$$|\psi(t)\rangle = \sum_n c_n(t)\,\exp(\mathrm{i}\Phi_n t)\,|\phi_n\rangle \tag{3.5}$$

where the $|\phi_n\rangle$ are the instantaneous eigenstates of the Hamiltonian $\hat{H}[\mathcal{E}(t)]$, and

$$\Phi_n = \frac{1}{\hbar}\int^t \mathrm{d}t'\,E_n(t'). \tag{3.6}$$

The equation of motion of $c_n(t)$ is

$$\dot{c}_n = \sum_{m\neq n} \frac{\langle\phi_n|\partial\hat{H}/\partial\mathcal{E}|\phi_m\rangle}{E_n - E_m}\dot{\mathcal{E}}\exp[\mathrm{i}(\Phi_n - \Phi_m)]\,c_m. \tag{3.7}$$

If E_n and $\langle\phi_n|\partial\hat{H}/\partial\mathcal{E}|\phi_m\rangle$ are assumed to be such slowly varying functions of $\mathcal{E}$ that they can be taken to be constant, and the c_n are small, the solution of (3.7) with the initial condition $c_n(0) = \delta_{nm}$ is

$$c_n(t) = -\mathrm{i}\hbar\frac{\langle\phi_n|\partial\hat{H}/\partial\mathcal{E}|\phi_m\rangle}{(E_n - E_m)^2}\dot{\mathcal{E}}\exp[\mathrm{i}(\omega_n - \omega_m)t] \tag{3.8}$$

with $\omega_n = E_n/\hbar$. In order to study the scattering process an incoming wavepacket with significant contributions only from states with energy close to E_0 is considered. In this case the matrix elements of $\partial\hat{H}/\partial\mathcal{E}$ can be set to a constant value V. We also assume that the perturbation varies slowly compared to the timescale of the interaction of the electron with the boundary: the rate of change $\dot{\mathcal{E}}$ can be considered to remain constant throughout the collision process. Using the definition of the evolution operator

$$\langle\phi_n|U(t)|\phi_m\rangle = \{c_n(t)|c_m(0) = \delta_{nm}\} \tag{3.9}$$

and defining the initial wavepacket as

$$|\psi(0)\rangle = \sum_n a_n|\phi_n\rangle \tag{3.10}$$

gives

$$E(t) = \langle\psi(t)|\hat{H}|\psi(t)\rangle = \langle\psi(0)|\hat{U}^\dagger(t)\hat{H}\hat{U}(t)|\psi(0)\rangle = \sum_n\sum_{n'} a_{n'}^* a_n \langle\phi_{n'}|\hat{U}^\dagger(t)\hat{H}\hat{U}(t)|\phi_n\rangle. \tag{3.11}$$

Use of the approximate expression for the elements of $\hat{U}$ obtained from (3.8) gives

$$E(t) = \sum_n |a_n|^2 E_n + \sum_n\sum_{n'\neq n} \frac{-\mathrm{i}\hbar\dot{\mathcal{E}}V a_{n'}^* a_n}{E_n - E_{n'}} \exp[\mathrm{i}(\omega_n - \omega_{n'})t]. \tag{3.12}$$

Converting the sums to integrals, we have

$$E(t) = E_0 - \mathrm{i}\rho^2\hbar\dot{\mathcal{E}}V \int \mathrm{d}E \int \mathrm{d}E' \frac{a(E)a^*(E')}{E - E'} \exp[\mathrm{i}(E - E')t/\hbar] \tag{3.13}$$

where E_0 is the initial energy of the wavepacket and ρ is the density of states (for each spin state). The normalization of the coefficients $a(E_n) \simeq a_n$ is

$$\int \mathrm{d}E\, |a(E)|^2 = \frac{1}{\rho}. \tag{3.14}$$

Differentiating (3.13) with respect to time gives

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \rho^2\dot{\mathcal{E}}V \int \mathrm{d}E \int \mathrm{d}E'\, a(E)a^*(E') \exp[\mathrm{i}(E - E')t/\hbar] \tag{3.15}$$

which can be integrated to give the total energy transferred during the interaction

$$\begin{aligned}\delta E &= \rho^2\dot{\mathcal{E}}V \int \mathrm{d}E \int \mathrm{d}E'\, a(E)a^*(E') \int_{-\infty}^{\infty} \mathrm{d}t \exp[\mathrm{i}(E - E')t/\hbar] \\ &= \pi\hbar\rho^2\dot{\mathcal{E}}V \int \mathrm{d}E\, |a(E)|^2 = 2\pi\hbar\rho\dot{\mathcal{E}}V.\end{aligned} \tag{3.16}$$

For the case of an externally applied sinusoidal field the function $\dot{\mathcal{E}}$ is given by $\mathcal{E}_0\omega\cos\omega t$ so that

$$\delta E = 2\pi\hbar\mathcal{E}_0\rho V\omega\cos\omega t. \tag{3.17}$$

3.3. Thomas–Fermi model for the screening potential

To calculate the energy absorbed by an electron colliding with the wall of the particle using (3.17), it is necessary to model the potential it experiences. A fully self-consistent calculation is not analytically tractable. The simplest model of the response of the electron gas to the field is the Thomas–Fermi model [4], which assumes, in accordance with (3.2), that the induced charge density is proportional to the potential, so that Laplace's equation reads

$$\frac{\partial^2 \delta V}{\partial z^2} = \frac{e^2 \delta n}{\epsilon_0} = \frac{3e^2 n}{2\epsilon_0 E_F} \delta V. \tag{3.18}$$

The solution of (3.18) is

$$\delta V(z) = V_0 \exp(-\alpha_s z). \tag{3.19}$$

The inverse screening length α_s can be obtained directly from (3.18) and V_0/α_s from (3.3):

$$\frac{V_0}{\alpha_s} = \frac{2\epsilon_0 \mathcal{E} E_F \cos\chi}{en} \qquad \alpha_s = \sqrt{\frac{3ne^2}{2\epsilon_0 E_F}} = \frac{2}{\sqrt{\pi a_0 \lambda_F}} \tag{3.20}$$

where a_0 is the Bohr radius and λ_F is the Fermi wavelength. We now compute the matrix elements of the potential $\delta V(z)$ between single-electron wavefunctions. The z dependence of the wavefunctions for the electrons trapped between planes at $z = 0$ and $z = L$ is

$$\psi_j(z) = \sqrt{2/L} \sin(j\pi z/L) \tag{3.21}$$

which gives matrix elements

$$\begin{aligned} V_{jj'} &= \frac{2V_0}{L} \int_0^L \mathrm{d}z \, \exp(-\alpha_s z) \sin\left(\frac{j\pi z}{L}\right) \sin\left(\frac{j'\pi z}{L}\right) \\ &\simeq \frac{V_0 \alpha_s}{L} \left(\frac{1}{\alpha_s^2 + (j-j')^2\pi^2/L^2} - \frac{1}{\alpha_s^2 + (j+j')^2\pi^2/L^2} \right) \end{aligned} \tag{3.22}$$

where the approximation $\alpha_s L \gg 1$ has been made, which corresponds to the short range of the screening potential compared to the separation of the planes. For states that are close in energy, $j \simeq j'$, and the required matrix element V can be obtained as

$$V = \frac{8mV_0 E_z}{L\alpha_s(\hbar^2\alpha_s^2 + 8mE_z)} = \frac{8mV_0 E_F \cos^2\phi}{L\alpha_s(\hbar^2\alpha_s^2 + 8mE_F\cos^2\phi)}. \tag{3.23}$$

Here $E_z = \hbar^2 j^2 \pi^2 / 2mL^2$ is the kinetic energy in the z direction, for a particle at the Fermi surface. This is related to the total energy E_F by $E_z = E_F \cos^2\phi$, where ϕ is the angle of incidence of the electron against the boundary.

The density of states (for each spin state) for a particle of energy E_z in a one-dimensional box is

$$\rho = \frac{mL}{\hbar\pi\sqrt{2mE_z}\cos\phi}. \tag{3.24}$$

Using the expression (3.20) for V_0/α_s, (3.17) now gives the energy transferred as the electron interacts with the wall as

$$\delta E = \frac{4E_F}{3env_F}\frac{\cos\phi}{(\Gamma+\cos^2\phi)}\frac{dq}{dt} = \frac{4\epsilon_0 E_F \omega \mathcal{E}_0 \cos\phi\cos\chi\cos\omega t}{env_F(\Gamma+\cos^2\phi)}. \tag{3.25}$$

Here Γ is a material dependent parameter given by

$$\Gamma = \frac{3n\hbar^2e^2}{16mE_F^2\epsilon_0} = \frac{2\lambda_F}{\pi a_0} = \frac{2^{5/3}}{3^{2/3}\pi^{4/3}}\frac{r_s}{a_0} \tag{3.26}$$

where r_s is the radius of a sphere defining the volume occupied by a conduction electron. Values of the parameter r_s/a_0 are tabulated in [4], and show that Γ is of the order of unity for ordinary metals. Comparing (3.20) and (3.26) it is clear that Γ is proportional to $(\lambda_F/\lambda_s)^2$, where $\lambda_s = 1/\alpha_s$ is the screening length. The energy transferred to the rebounding electron is reduced when Γ is large, because in this limit only the tail of the wavefunction penetrates into the region where the potential $\delta V(z)$ differs significantly from zero.

Equation (3.25) is the principal result of this section. It is instructive to compare this with the predictions of a purely classical analysis, in which the change in energy of an electron bouncing off a surface with potential $\delta V(z,t)$ is

$$\delta E = \int dt\,\frac{\partial H}{\partial t} = \frac{2}{v_F\cos\phi}\int dz\,\frac{\partial \delta V}{\partial t} = \frac{2}{v_F\cos\phi}\frac{\partial}{\partial t}\int dz\,\delta V. \tag{3.27}$$

Using (3.3), we find

$$\delta E = \frac{4E_F}{3nev_F}\frac{1}{\cos\phi}\frac{dq}{dt}. \tag{3.28}$$

This result has an unphysical divergence at $\phi = \frac{1}{2}\pi$, corresponding to the electron sampling the potential δV for a long time if it strikes the boundary at glancing incidence. The more realistic quantum model (3.25) does not have this divergence, but at all angles other than $\phi = \frac{1}{2}\pi$, the quantum expression approaches the classical value in the limit $\Gamma \to 0$.

4. Ballistic electrons in a smooth walled sphere

We now consider the calculation of the energy absorption in the case where the electrons move ballistically inside a spherical boundary, and are reflected specularly at the walls. First we discuss briefly the classical dynamics of the electrons.

The trajectories of the electrons are confined to planes that contain the centre of the sphere. The motion of an electron in one of these planes is a typical example of integrable motion for a system with two degrees of freedom [6]. In such a system a canonical transformation can be found that maps the phase space coordinates (x', y', p'_x, p'_y) into another set of coordinates (θ, θ', J, I), termed action angle variables, such that the Hamiltonian is independent of the coordinates θ, θ'. The conjugate momenta J and I are therefore constants of motion. For motion in the sphere, the Hamiltonian is independent of the polar angle θ in the (x', y') plane, and the conjugate momentum is the angular momentum, $J = x'p'_y - y'p'_x$. We will not need to characterize the remaining action angle variables (I, θ') for the radial motion in any detail.

The motion of any given electron can be described by a vector angular momentum $\boldsymbol{J}$, which is normal to the (x', y') plane and has magnitude J. The set of six variables consisting of the energy E, the angular momentum $\boldsymbol{J} = (J_x, J_y, J_z)$ and the two angle variables θ, θ' uniquely specify the phase space coordinates of an electron. In order to evaluate the energy absorption using (2.6), we must perform an integration over the energy surface (the level surface of E). This integration is most conveniently carried out using the coordinate system described above. In appendix A we show that the measure $\mathrm{d}\alpha$ of phase space volume is

$$\mathrm{d}\alpha = \mathrm{d}\Sigma\,\mathrm{d}E = (\tau/J)\,\mathrm{d}E\,\mathrm{d}\theta\,\mathrm{d}\theta'\,\mathrm{d}J_x\,\mathrm{d}J_y\,\mathrm{d}J_z \tag{4.1}$$

where τ is the period between bounces.

We now calculate the total energy $\Delta E_T(t)$ absorbed in time t by summing the contributions δE for each bounce of each electron. The energy $\Delta E(t)$ absorbed by a given electron can be obtained as a sum of the energies transferred in each collision. Using the expression (3.25) for the energy transferred in a single collision gives

$$\Delta E(t) = \sum_{n=1}^{N} \delta E = \frac{A\cos\phi}{\Gamma + \cos^2\phi} \sum_{n=1}^{N} \cos\chi_n \cos\omega t_n \tag{4.2}$$

where $N \simeq t/\tau$ is the number of collisions with the wall, χ_n is the polar angle of the nth reflection, occurring at time t_n, relative to the direction of the electric field (the z axis), and $A = 4\epsilon_0 E_F \omega \mathcal{E}/env_F$. Some elementary geometry shows that we can write

$$\cos\chi_n = \sin\Theta\cos\theta_n \tag{4.3}$$

where θ_n is the polar angle of the nth reflection measured in the plane containing the electron trajectory, and Θ is the angle between the vector $\boldsymbol{J}$ and the z axis. These angles are illustrated in figure 3, from which it can be seen that θ_n is given by $\theta_n = 2n(\pi/2-\phi)+\theta_0 = 2n\phi' + \theta_0$. Use of these expressions and $t_n = n\tau$ gives

$$\Delta E(t) = \frac{A\cos\phi\sin\Theta}{\Gamma + \cos^2\phi} \sum_{n=1}^{N} \cos(2n\phi' + \theta_0)\cos n\omega\tau. \tag{4.4}$$

The sum can be written in the form

$$\begin{aligned}
\tfrac{1}{2}\sum_{n=1}^{N}[\cos(2n\phi'+\theta_0-n\omega\tau)+\cos(2n\phi'+\theta_0+n\omega\tau)] &= \tfrac{1}{2}\sum_{n=1}^{N}[\cos(n\delta\theta_1+\theta_0)+\cos(n\delta\theta_2+\theta_0)] \\
&= \tfrac{1}{2}\,\mathrm{Re}\exp(\mathrm{i}\theta_0)\sum_{n=1}^{N}[\exp(\mathrm{i}n\delta\theta_1)+\exp(\mathrm{i}n\delta\theta_2)] \\
&= \tfrac{1}{2}\,\mathrm{Re}\,\frac{\exp(\mathrm{i}\theta_0)[1-\exp(\mathrm{i}N\delta\theta_1)]}{1-\exp(\mathrm{i}\delta\theta_1)} + \tfrac{1}{2}\,\mathrm{Re}\,\frac{\exp(\mathrm{i}\theta_0)[1-\exp(\mathrm{i}N\delta\theta_2)]}{1-\exp(\mathrm{i}\delta\theta_2)}
\end{aligned} \tag{4.5}$$

where Re denotes the real part, $\delta\theta_1 = 2\phi' - \omega\tau$ and $\delta\theta_2 = 2\phi' + \omega\tau$.

It can be seen that a resonance can occur in expression (4.5) if $\delta\theta_1$ or $\delta\theta_2$ is close to a multiple of 2π. These resonances will dominate the response of the system to the field. In

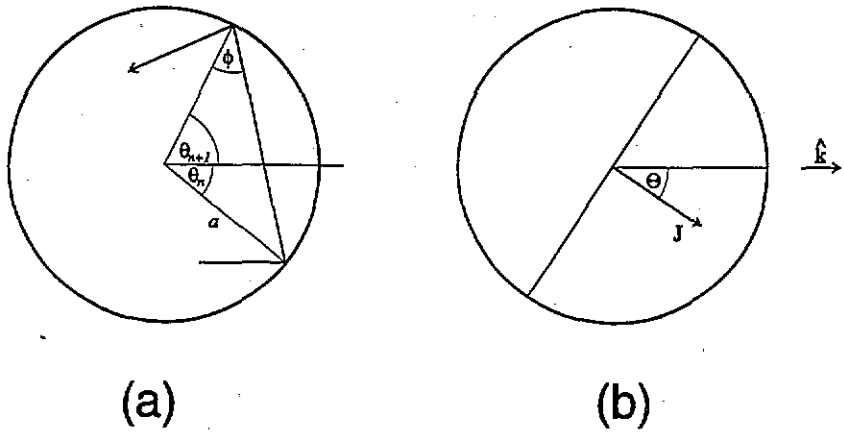

Figure 3. (*a*) In the smooth walled sphere, the electron motion is confined to planes. The polar angles in the plane of motion of successive impacts are θ_n. (*b*) The plane of motion is tilted at an angle $\frac{1}{2}\pi - \Theta$ with respect to the direction of the electric field.

order to proceed further, it is necessary to study the possible resonance solutions. For the first term the condition for the kth resonance is

$$2\phi'_k + 2k\pi = (2\omega a/v_F)\sin\phi'_k. \tag{4.6}$$

Since $\frac{1}{2}\pi - \phi'_k$ is the angle between the electron direction and the normal to the particle surface, we have $0 \leqslant \phi'_k \leqslant \frac{1}{2}\pi$, and k can take the values $0, 1, 2, \ldots$. In order to understand the solutions of (4.6) it is convenient to re-write it in the form

$$(v_F/a\omega)(\phi'_k + k\pi) = \sin\phi'_k. \tag{4.7}$$

For $k = 0$ and small ϕ', examination of (4.7) shows that there are no solutions below $\omega_c = v_F/a$. Above ω_c one or more solutions exist; as ω increases the intercepts $v_F k\pi/a\omega$ move closer to the origin and the number of solutions increases. By substituting $\phi'_k = \frac{1}{2}\pi$, $\sin\phi'_k = 1$ into (4.7) it can be seen that the condition for the kth solution to exist is $\omega \geqslant v_F\pi(2k+1)/2a$. When ω is sufficiently large, the solutions ϕ'_k effectively form a continuum with all values of ϕ' allowed; the condition for this to occur can be seen to be that ω is large compared to $\pi\omega_c$. For the second term of (4.5) the analysis of the solutions can be performed in a similar manner; the analogue of (4.7) is

$$(v_F/a\omega)(k\pi - \phi'_k) = \sin\phi'_k. \tag{4.8}$$

Solutions of (4.8) can be found for $k \geqslant 1$. The construction of the solutions to (4.7) and (4.8) is illustrated in figure 4. The condition for the kth solution of (4.8) to exist is $\omega \geqslant v_F\pi(2k-1)/2a$. Solutions of (4.7) and (4.8) only coincide if $\phi' = 0$ or $\phi' = \frac{1}{2}\pi$.

The solutions of (4.7) will be considered first. By defining $\delta\theta'_{1k} = \delta\theta_1 + 2k\pi$, it can be seen that near resonance, when $\delta\theta'_{1k}$ is small, the denominator of the first term in the last line of (4.5) can be approximated by $i\delta\theta'_1$ whilst the second non-resonant term is negligible in comparison to the first. Equation (4.5) becomes

$$\frac{1}{2\delta\theta'_{1k}}\,\mathrm{Im}\exp(i\theta_0)[1 - \exp(iN\delta\theta'_{1k})] = \frac{1}{2\delta\theta'_{1k}}[\sin\theta_0 - \sin(\theta_0 + N\delta\theta'_{1k})] \tag{4.9}$$

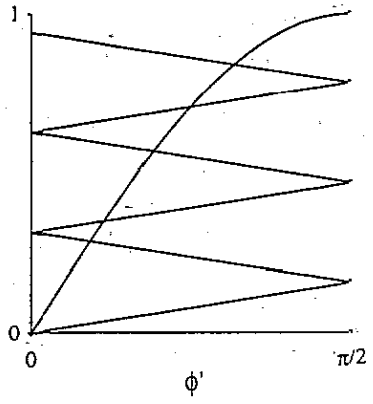

Figure 4. Illustration of the allowed solutions of (4.7) and (4.8). The solutions ϕ^* correspond to the intersections of the straight lines with the curve $y = \sin\phi$. The example shown is for $\omega = 10\omega_c$.

where Im denotes the imaginary part. Substituting into (4.4) gives

$$\Delta E(t) = \frac{A\cos\phi\sin\Theta}{2\delta\theta'_{1k}(\Gamma+\cos^2\phi)}[\sin\theta_0 - \sin(\theta_0 + N\delta\theta'_{1k})] \tag{4.10}$$

where $N = t/\tau$. The average required to calculate the energy absorbed using (2.6) is obtained by averaging over the initial angle θ_0 and the angular momentum J. Performing the integral over J is equivalent to integrating over ϕ' and therefore to summing over the resonances. The average of the square of (4.10) over θ_0 is

$$\Delta E^2(t) = \frac{A^2\cos^2\phi\sin^2\Theta g(\delta\theta'_{1k})}{2(\Gamma+\cos^2\phi)^2} \tag{4.11}$$

where

$$g(\delta\theta'_{1k}) = \frac{\sin^2(N\delta\theta'_{1k}/2)}{(\delta\theta'_{1k})^2}. \tag{4.12}$$

The integral over J is

$$\langle\Delta E^2(t)\rangle = A^2\sum_{k=0}^{k_{max}}\int \mathrm{d}J\,\mu(J)\frac{\cos^2\phi\sin^2\Theta g(\delta\theta'_{1k})}{2(\Gamma+\cos^2\phi)^2}\Big/\int \mathrm{d}J\,\mu(J) \tag{4.13}$$

where $\mu(J) = \tau/J = 2a\cos\phi/Jv_F$ (see appendix A). Using $J = mav_F\sin\phi$, the integral in the denominator is

$$8\pi a^3m^2v_F\int_0^{\pi/2}\mathrm{d}\phi\,\cos^2\phi\sin\phi = \frac{8\pi a^3m^2v_F}{3}. \tag{4.14}$$

Similarly, the integral in the numerator is

$$\frac{8\pi A^2m^2a^3v_F}{3}\sum_{k=0}^{k_{max}}\int_0^{\pi/2}\mathrm{d}\phi'\frac{\sin^4\phi'\cos\phi'}{(\Gamma+\sin^2\phi')^2}\frac{\sin^2[t(2\phi'-\omega\tau+2k\pi)/2\tau]}{(2\phi'-\omega\tau+2k\pi)^2}. \tag{4.15}$$

Denoting the integral over ϕ' for the kth resonance as I_k and making the substitution

$$y = \frac{(2\phi' - \omega\tau + 2k\pi)t}{2\tau} = \frac{t}{2}\left(\frac{v_F\phi'}{a\sin\phi'} - \omega + \frac{k\pi v_F}{a\sin\phi'}\right) \tag{4.16}$$

gives

$$I_k = \frac{v_F t}{8a}\int \mathrm{d}y\, f_1(\phi')\frac{\sin^2 y}{y^2} \tag{4.17}$$

with

$$f_1(\phi') = \frac{\pm\sin^4\phi'\cos\phi'}{(\Gamma + \sin^2\phi')^2[\sin\phi' - (\phi' + k\pi)\cos\phi']} \tag{4.18}$$

where the + sign is used for $k = 0$ and the − sign otherwise. For large t, $\partial\phi'/\partial y$ is very small, and the function $f(\phi')$ can be taken out of the integral in (4.17):

$$I_k = \frac{v_F t f_1(\phi_k^*)}{8a}\int_{-\infty}^{\infty}\mathrm{d}y\,\frac{\sin^2 y}{y^2} \tag{4.19}$$

where ϕ_k^* is the solution of (4.7). Note that, despite the close similarity to the derivation of the Fermi golden rule, we are dealing here with a classical rather than a quantum resonance phenomenon. The value of the integral in (4.19) is π; collecting the multiplying factors together and summing over all solutions gives

$$\langle\Delta E^2(t)\rangle = \frac{2\pi\epsilon_0^2 E_F^2\omega^2\mathcal{E}_0^2 t}{v_F e^2 n^2 a}\sum_{k=0}^{k_{max}} f_1(\phi_k^*). \tag{4.20}$$

By using (4.7) it is possible to express $f_1(\phi_k^*)$ in the form

$$f_1(\phi_k^*) = \frac{\sin^3\phi_k^*\cos\phi_k^*}{(\Gamma + \sin^2\phi_k^*)^2(1 - \lambda\cos\phi^*)} \tag{4.21}$$

with $\lambda = \omega a/v_F$. Using (2.6) and (2.8) gives

$$\frac{\mathrm{d}E_T}{\mathrm{d}t} = \frac{2\epsilon_0^2 E_F^2 m^2\omega^2\mathcal{E}_0^2 a^2}{3e^2 n^2\hbar^3}\sum_{k=0}^{k_{max}} f_1(\phi_k^*) \tag{4.22}$$

which includes all the resonances satisfying (4.7).

Repeating the analysis for the second set of resonances (4.8) gives an expression with the same form (4.21) but with a function $f_2(\phi^*)$ obtained from f_1 by changing the sign of λ. The final form of $\mathrm{d}E_T/\mathrm{d}t$ is therefore

$$\frac{\mathrm{d}E_T}{\mathrm{d}t} = \frac{2\epsilon_0^2 E_F^2 m^2\omega^2\mathcal{E}_0^2 a^2}{3e^2 n^2\hbar^3}\left(\sum_{k_1=0}^{k_{1max}} f_1(\phi_{k1}^*) + \sum_{k_2=1}^{k_{2max}} f_2(\phi_{k2}^*)\right). \tag{4.23}$$

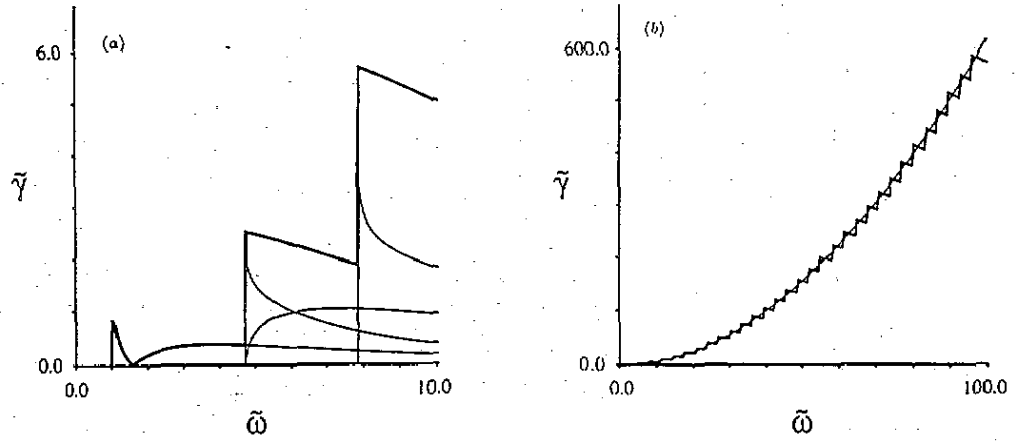

Figure 5. Absorption coefficient as a function of frequency for a smooth sphere with specular reflection with $\Gamma = 1$. Figure 5(a) shows the individual resonance bands up to $k = 2$ corresponding to solutions of (4.7) and (4.8) and the total absorption coefficient (bold curve) obtained by adding the contributions of these bands. Figure 5(b) shows the effect of many overlapping resonances to produce the limiting quadratic behaviour. Scaled units are used such that $\tilde{\omega} = \omega/\omega_c$, and the asymptotic form (4.27) is $\tilde{\gamma} = \tilde{\omega}^2 F(\Gamma)$.

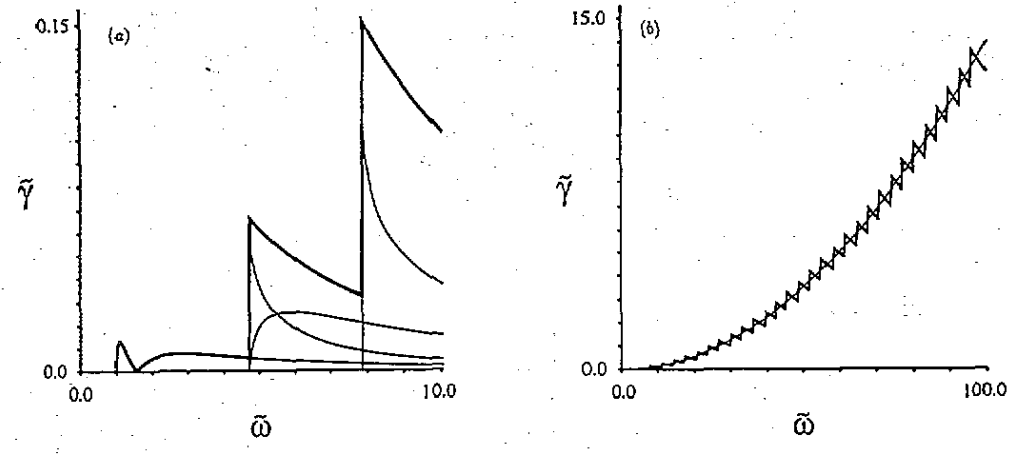

Figure 6. As figure 5 with $\Gamma = 10.0$.

The number of allowed solutions increases as ω increases, as discussed above. The absorption coefficient has a low-frequency cut-off at ω_c and consists of a series of overlapping bands at frequencies above $v_F\pi/a$. The form of the bands obtained from a numerical solution of (4.7) and (4.8) is illustrated in figures 5 and 6. The lowest-frequency absorption band corresponds to a circumferential orbit at its low-frequency end, and a diagonal bounce at its high-frequency cut-off. All of the other bands have no upper cut-off. The absorption coefficient displays an oscillatory structure, reminiscent of that predicted by Gorkov and Eliashberg [13] in the vicinity of ω_0, although the physical mechanism,

resonances between the electron bounce frequency and the field frequency, is completely different. Such resonances arise from the regularity of the classical motion and would be anticipated to occur in any system in which the electron dynamics is integrable. It should also be noted that our results show that the effective conductivity *ansatz* (described in section 1.2) is oversimplified. The geometrical resonance effects as displayed in figures 5 and 6 are more complex than the ω^2 behaviour predicted by this model, and the absorption coefficient is also a function of the material dependent parameter Γ.

In the continuum limit $\omega \gg \omega_c$, the sum over the bands can be obtained in analytic form. Converting the sum over k (4.23) to an integral over ϕ' gives

$$\sum_k f(\phi_k^*) = \frac{1}{\pi}\int_0^{\pi/2} d\phi' \frac{\sin^3\phi' \cos\phi'}{(\Gamma + \sin^2\phi')^2} = \frac{1}{\pi}F(\Gamma) \tag{4.24}$$

for both f_1 and f_2. The integral is independent of ω, so from (4.22) the absorption coefficient is proportional to ω^2 in this region. Using (4.22) and (4.24) dE_T/dt can be written

$$\frac{dE_T}{dt} = \frac{4\epsilon_0^2 E_F^2 m^2 \omega^2 \mathcal{E}_0^2 a^2}{3\pi e^2 n^2 \hbar^3} F(\Gamma). \tag{4.25}$$

By making the successive substitutions $x = \sin\phi'$, $y = x^2$, $F(\Gamma)$ can be calculated:

$$F(\Gamma) = \frac{1}{2}\int_0^1 dy \frac{y}{(\Gamma + y)^2} = \frac{1}{2}\left[\ln\left(\frac{(1+\Gamma)}{\Gamma}\right) - \frac{1}{(1+\Gamma)}\right]. \tag{4.26}$$

It is also possible to obtain the sum over the resonances by an alternative method in the limit where the resonances are dense in ϕ, by using a formalism in which sucessive bounces are considered to be uncorrelated. This calculation is described in appendix B.

We conclude this section by making a direct comparison between the absorption coefficient obtained from (4.25) and that obtained from the Mie theory using the effective conductivity *ansatz*. Substituting (4.25) into (2.9) gives

$$\gamma = \frac{9\pi^2 \mathcal{F}\omega^2 \epsilon_0 \hbar^3}{8e^2 acm E_F} F(\Gamma). \tag{4.27}$$

The Mie theory gives the expression [2]

$$\gamma = 9\mathcal{F}\omega^2\epsilon_0/4\pi\sigma c \tag{4.28}$$

where σ is the conductivity. The expression generally used for comparing (4.28) with experiment is obtained by using the Drude conductivity $\sigma = ne^2\tau/m$; for a ballistic system the relaxation time τ is set equal to the bounce time a/v_F. With these substitutions (4.28) becomes

$$\gamma = 27\pi\mathcal{F}\omega^2\epsilon_0\hbar^3/8e^2 acm E_F. \tag{4.29}$$

Comparing (4.27) and (4.29), it can be seen that the predicted dependence on particle radius, Fermi energy and effective mass is identical and the numerical prefactors are very similar. However the function $F(\Gamma)$ in (4.27) introduces an extra material dependent multiplier, and reduces the predicted absorption coefficient considerably compared to (4.29). (The function $F(\Gamma)$ is ~ 0.1 for $\Gamma = 1$ and $\sim 2 \times 10^{-3}$ for $\Gamma = 10$.)

5. Ballistic electrons in a rough walled sphere

Unlike the smooth walled case, there is no unique definition of the electron dynamics in a rough walled particle. We will consider one specific model which represents an extreme degree of roughness. We were not able to find any analytically tractable and physically reasonable model with a variable degree of 'roughness', which would interpolate continuously between this limit and the smooth walled case.

There is a complication that arises in the case of a rough walled particle, namely that the surface charge density will be concentrated at 'prominences' on the surface, and will be very small inside 'pits' (see figure 7(a)). It would be a formidable task to obtain a general model for this non-uniform charge distribution in terms of the statistical topography of the surface. Instead we use a specific model which is analytically tractable. The model we use is illustrated in figure 7(b): the particle has a large number of randomly placed 'whiskers' protruding from its surface, which are tall enough, in relation to their typical separation, that the induced surface charge density is confined to the tips of the whiskers.

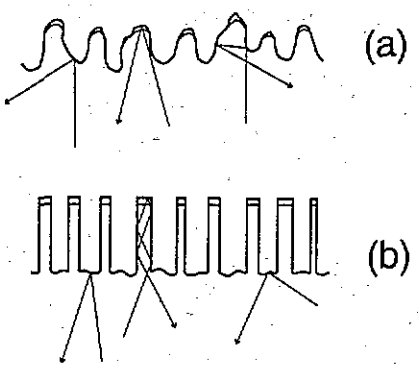

Figure 7. On a rough surface (a), the surface charge is concentrated on prominences. We consider a model (b) in which the surface charge is concentrated at the tips of 'whiskers', which occupy a fraction η of the surface area.

An electron approaching the boundary will often be scattered back into the interior of the particle without reaching the exterior surface itself. From (3.25), we see that only those electrons which reach the exterior surface, where the charge density q resides, can have their energies modified by the interaction with the wall. This feature of the model simulates the effect of the non-uniform distribution of charge density in figure 7(a): in both models, many of the electrons colliding with the wall rebound with their energies unchanged.

If the fraction of the surface occupied by the 'whiskers' is η, the surface charge density within the 'whiskers' is increased by a factor $1/\eta$. From (3.25), it follows that the energy transferred to an electron is increased by a factor $1/\eta$ for each bounce in which the electron penetrates to the end of a whisker, and the energy transfer is zero for the other bounces.

Even for a rough walled sphere, the positions of the successive bounces are correlated: it is clear that the successor of a given bounce is more likely to be in the opposite hemisphere than the same hemisphere. If the surface is rough, widely separated bounces may be assumed to be uncorrelated. If the density of whiskers η is small, the bounces upon which the electron penetrates to the end of a whisker, and rebounds with a changed energy, will

almost all be widely separated, and their positions can therefore be regarded as uncorrelated. We can therefore write

$$\langle \Delta E^2(t) \rangle = \sum_{j=1}^{N} \sum_{j'=1}^{N} \langle \delta E_j \delta E_{j'} \rangle = \sum_{j=1}^{N} \langle \delta E_j^2 \rangle = N \langle \delta E^2 \rangle \tag{5.1}$$

where $\Delta E(t)$ is the energy transferred to an electron in time t, δE is the energy transfer at an individual bounce, and N is the expected number of bounces resulting in a transfer of energy occurring in time t. The average in (5.1) is taken over all possible positions of the bounces, with all possible angles of incidence.

The number of bounces occurring in (5.1) is $N = \eta t / \langle \tau \rangle$, where $\langle \tau \rangle$ is the mean interval between bounces for ergodic motion; the factor of η accounts for the fact that most bounces do not result in any energy transfer. The mean interval $\langle \tau \rangle$ is

$$\begin{aligned} \langle \tau \rangle &= \frac{1}{\Omega(E)} \int \mathrm{d}\alpha \, \tau \, \delta(E - H(\alpha)) = \int \mathrm{d}J \, \mu(J) \, \tau \Big/ \int \mathrm{d}J \, \mu(J) \\ &= \int_0^{mav_F} \mathrm{d}J \, J \, \tau^2 \Big/ \int_0^{mav_F} \mathrm{d}J \, J \, \tau \\ &= \frac{2a}{v_F} \int_0^{\pi/2} \mathrm{d}\phi \, \sin\phi \cos^3\phi \Big/ \int_0^{\pi/2} \mathrm{d}\phi \, \sin\phi \cos^2\phi = \frac{3a}{2v_F} \end{aligned} \tag{5.2}$$

where we have used (4.1) and $J = mav_F \sin\phi$, $\tau = (2a/v_F)\cos\phi$.

The expression for $\langle \delta E^2 \rangle$ is similar in form to (3.24), apart from dimensionless geometrical factors, but contains a factor $1/\eta^2$ to account for the enhanced surface charge; hence

$$\langle \delta E^2 \rangle = \frac{A^2}{\eta^2} \langle \cos^2 \omega t \rangle \langle \cos^2 \chi \rangle \left\langle \frac{\cos^2\phi}{(\Gamma + \cos^2\phi)^2} \right\rangle. \tag{5.3}$$

The average over ϕ is performed in the same way as for (5.2)

$$\left\langle \frac{\cos^2\phi}{(\Gamma + \cos^2\phi)^2} \right\rangle = \int_0^{mav_F} \mathrm{d}J \, \tau \, J \, \frac{\cos^2\phi}{(\Gamma + \cos^2\phi)^2} \Big/ \int_0^{mav_F} \mathrm{d}J \, \tau \, J = 3G(\Gamma) \tag{5.4}$$

where

$$G(\Gamma) = \int_0^{\pi/2} \mathrm{d}\phi \, \frac{\sin\phi \cos^4\phi}{(\Gamma + \cos^2\phi)^2} \tag{5.5}$$

can be expressed in terms of a hypergeometric function [24].

Setting $\langle \cos^2 \omega t \rangle = 1/2$, $\langle \cos^2 \chi \rangle = 1/3$, using these results with (2.6) and (2.8), and substituting for A gives

$$\frac{\mathrm{d}E_T}{\mathrm{d}t} = \frac{32\epsilon_0^2 E_F^2 m^2 \omega^2 \mathcal{E}_0^2 a^2}{9\pi\eta e^2 n^2 \hbar^3} G(\Gamma). \tag{5.6}$$

The absorption coefficient is proportional to ω^2 at all frequencies; there is no low-frequency cut-off as is found for the smooth sphere. The effect of the factor of $1/\eta$ is to considerably enhance the absorption coefficient compared to that for a smooth sphere. This enhancement, which is due to the increased charge density on surface prominences, will be a feature of any model for a rough sphere. It could play a role in explaining the anomalously large absorption coefficients that are often observed in suspensions of small metallic particles [25]. Other models, typically involving clustering of particles, have also been proposed to explain this effect; references are given in [25].

6. Semiclassical model for absorption above the plasma frequency

In this section we present a semiclassical theory for the absorption of radiation at frequencies above the plasma frequency. This problem was originally treated by Kawabata and Kubo [10], who gave a fully quantum mechanical analysis. They found that the absorption depends on the parameter $\nu = \hbar\omega/E_F$ which is related to the parameter Γ introduced in section 3 for the free electron model

$$\nu^2 = \tfrac{16}{3}(\omega/\omega_p)^2\Gamma. \tag{6.1}$$

Our semiclassical method is only applicable in the limit $\nu \to 0$, and it therefore would not be relevant to any real system. We include this calculation because we feel it gives useful physical insight, and because the correspondence with the fully quantum calculation, in the regime in which the theories overlap, is reassuring.

At frequencies above ω_p the electric field penetrates the interior of the particle. Because the plasma frequency is much higher than the bounce frequency ω_c, the electron is accelerated and decelerated many times as it traverses the particle; the change in the momentum in the direction of the applied field oscillates cosinusoidally:

$$\delta p = (e\mathcal{E}_0/\omega)\hat{k}\cos\omega t \tag{6.2}$$

where $\hat{k}$ is a unit vector in the direction of the electric field. There is a corresponding oscillation of the energy of the electron about its mean value.

The mean value about which these oscillations occur changes when the electron strikes the wall of the particle. Consider what happens when an electron strikes the boundary of the particle at time t^*. The instant before it strikes the wall the momentum of the electron is

$$p = p_0 + \delta p = p_0 + (e\mathcal{E}_0/\omega)\hat{k}\cos\omega t^*. \tag{6.3}$$

The instant after the impact its momentum is

$$p' = \mathcal{R}p_0 + (e\mathcal{E}_0/\omega)\mathcal{R}\hat{k}\cos\omega t^* \tag{6.4}$$

where $\mathcal{R}x$ is the vector obtained by specular reflection of the vector x (figure 8). After the impact, the time dependence of the momentum of the electron is given by

$$p = p_0' + (e\mathcal{E}_0/\omega)\hat{k}\cos\omega t \tag{6.5}$$

i.e. the momentum oscillates about a new mean value p_0'. Setting $t = t^*$ in (6.5), and equating with (6.4), we find

$$p_0' = \mathcal{R}p_0 + (e\mathcal{E}_0/\omega)(\mathcal{R}\hat{k} - \hat{k})\cos\omega t^* = \mathcal{R}p_0 + (2e\mathcal{E}_0/\omega)(\hat{k}\cdot\hat{n})\hat{n}\cos\omega t^* \tag{6.6}$$

where $\hat{n}$ is the inward unit vector normal to the boundary at the point of impact. The change in the mean energy of the electron after the collision is

$$\delta E = (p_0'^2 - p_0^2)/2m = (-2e\mathcal{E}_0/m\omega)(\hat{k}\cdot\hat{n})(p_0\cdot\hat{n})\cos\omega t^*. \tag{6.7}$$

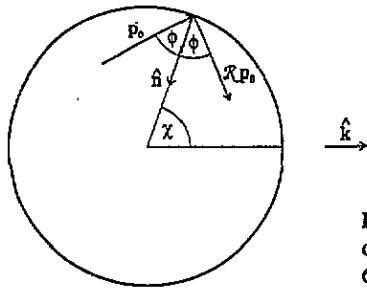

Figure 8. Illustration of vectors used in the discussion of the response above the plasma frequency in section 6.

We must sum the contributions δE to the change in the energy of an electron given by (6.7). First we specialize this formula to the case of a spherical boundary. The factor $(p_0 \cdot \hat{n})$ is equal to $mv\cos\phi$, where ϕ is the angle of incidence of the electron. The factor $(\hat{k} \cdot \hat{n})$ is equal to $\cos\chi_n$, which is given by (4.3). The energy transferred in a single collision is therefore

$$\delta E_n = (2ev\mathcal{E}_0/\omega)\cos\phi\sin\Theta\cos\theta_n\sin\omega t_n. \tag{6.8}$$

The absorption coefficient can be obtained as a sum of resonance terms as described in section 4. Because ω is very large compared to the bounce frequency, the resonances are dense in ϕ, and the discussion of appendix B shows that we are justified in treating these δE as a set of uncorrelated random variables. The total change in the energy of a given electron is therefore treated as a random variable with mean value zero and with variance

$$\begin{aligned}\langle\Delta E^2(J)\rangle &= \left\langle\left(\sum_{n=1}^{N}\delta E_n\right)^2\right\rangle = \frac{t}{\tau}\left(\frac{2ev\mathcal{E}_0}{\omega}\right)^2\cos^2\phi\sin^2\Theta\left\langle\frac{1}{N}\sum_{n=1}^{N}\cos\theta_n\sin\omega t_n\right\rangle^2 \\ &= \frac{t}{\tau}\left(\frac{ev\mathcal{E}_0}{\omega}\right)^2\cos^2\phi\sin^2\Theta\end{aligned} \tag{6.9}$$

where we have approximated the number of bounces by $N \simeq t/\tau$. To find the total energy absorbed using (2.6) we must compute $\langle\Delta E^2\rangle$, the variance of the change of the single-electron energies averaged over the whole of the energy shell. The average over the angle variables θ and θ' has already been computed in (6.9). It remains to average over the angular momentum J: using the measure (4.1), we find

$$\langle\Delta E^2\rangle = \int \mathrm{d}J\,\frac{\tau}{J}\langle\Delta E^2(J)\rangle \Big/ \int \mathrm{d}J\,\frac{\tau}{J}. \tag{6.10}$$

The denominator of this expression was evaluated in (4.14). The numerator is

$$\begin{aligned}&2\pi\int_0^{\pi}\mathrm{d}\Theta\,\sin^3\Theta\int_0^{J_{\max}}\mathrm{d}J\,J\cos^2\phi \\ &\quad= \frac{8\pi}{3}\int\mathrm{d}J\,J\cos^2\phi = \frac{8\pi m^2a^2v_F^2}{3}\int_0^{\pi/2}\mathrm{d}\phi\,\cos^3\phi\sin\phi = \frac{4\pi m^2a^2v_F^2}{3}.\end{aligned} \tag{6.11}$$

The result for $\langle\Delta E^2\rangle$ is

$$\langle\Delta E^2\rangle = e^2\mathcal{E}_0^2v_F^3t/4\omega^2a. \tag{6.12}$$

Substituting this result and the expression for the density of states at E_F (2.8) into (2.6), the rate of change of energy is found to be

$$\frac{dE_T}{dt} = \frac{2e^2\mathcal{E}_0^2 a^2 E_F^2}{3\pi\hbar^3\omega^2}. \tag{6.13}$$

This can be directly compared with the quantum mechanical calculation [12] using the Kawabato–Kubo method. ([12] corrects errors in the original paper [10].) The quantum mechanical result for the imaginary part $\epsilon_2(\omega)$ of the dielectric constant is

$$\epsilon_2(\omega) = \frac{4e^2E_F^3}{\pi\hbar^4\omega^4 a} H(\hbar\omega/E_F). \tag{6.14}$$

In the semiclassical limit $\nu = \hbar\omega/E_F \ll 1$, the expression given in [12] for $H(\nu)$ has the property $H(\nu) \sim \nu$ as $\nu \to 0$. In this limit we therefore have $\epsilon_2(\omega) = 4e^2E_F^2/\pi\hbar^3\omega^3 a$. Using the relationships

$$\epsilon_2 = (4\pi/\omega)\sigma \tag{6.15}$$

where σ is the conductivity, and

$$dE_T/dt = \tfrac{1}{2}\sigma\mathcal{E}_0^2\mathcal{V} \tag{6.16}$$

where $\mathcal{V}$ is the volume of the particle, gives an expression identical to (6.13).

Our semiclassical computations are only valid if the quantum energy $\hbar\omega$ is small compared to the Fermi energy E_F. Because the calculation applies when $\omega \gg \omega_p$, we must have $\nu_p = \hbar\omega_p/E_F \ll 1$ for the theory to be applicable, whereas ν_p is of the order of unity for most metals, and is large in materials with fewer charge carriers. Unlike the quantum mechanical calculations, which require expressions for the wavefunctions, our calculation can readily be generalized to other particle shapes with either integrable or chaotic classical motion.

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Appendix A

In this appendix we show that the Jacobean K of the transformation between the canonical phase space coordinates $(\boldsymbol{r}, \boldsymbol{p}) = (x, y, z, p_x, p_y, p_z)$ and the set of coordinates $(\theta, \theta', J_x, J_y, J_z, E)$ is

$$K = \frac{\partial(x, y, z, p_x, p_y, p_z)}{\partial(\theta, \theta', J_x, J_y, J_z, E)} = \frac{\tau}{J}. \tag{A.1}$$

The electron orbits are confined to planes containing the origin with coordinates (x', y'), and corresponding momenta (p_x', p_y'). The primed and un-primed coordinates are related by rotation matrices:

$$\boldsymbol{r} = \tilde{R}(\Theta, \Phi)\boldsymbol{r}' \qquad \boldsymbol{p} = \tilde{R}(\Theta, \Phi)\boldsymbol{p}' \qquad \tilde{R}(\Theta, \Phi) = \tilde{R}_z(\Phi)\tilde{R}_y(\Theta) \tag{A.2}$$

where $\tilde{R}_y(\Phi)$ and $\tilde{R}(\Theta)$ are rotations about the y and z axes, so that

$$\tilde{R}(\Theta, \Phi) = \begin{pmatrix} \cos\Theta\cos\Phi & \sin\Phi & \sin\Theta\cos\Phi \\ -\cos\Theta\sin\Phi & \cos\Phi & -\sin\Theta\sin\Phi \\ -\sin\Theta & 0 & \cos\Theta \end{pmatrix}. \tag{A.3}$$

Note that Θ and Φ are polar cooordinates for the direction of the angular momentum vector, i.e. $(J_x, J_y, J_z) = (J\sin\Theta\sin\Phi, J\sin\Theta\cos\Phi, J\cos\Theta)$, and therefore

$$\mathrm{d}J_x\,\mathrm{d}J_y\,\mathrm{d}J_z = J^2\sin\Theta\,\mathrm{d}J\,\mathrm{d}\Theta\,\mathrm{d}\Phi. \tag{A.4}$$

Setting $z' = p'_z = 0$, we obtain the following transformation between the $(\boldsymbol{r}, \boldsymbol{p})$ coordinates and the $(x', y', p'_x, p'_y, \Theta, \Phi)$ coordinates:

$$\boldsymbol{r} = \tilde{R}(\Theta, \Phi)\begin{pmatrix} x' \\ y' \\ 0 \end{pmatrix} \qquad \boldsymbol{p} = \tilde{R}(\Theta, \Phi)\begin{pmatrix} p'_x \\ p'_y \\ 0 \end{pmatrix}. \tag{A.5}$$

Computing the Jacobean K_1 of this transformation, we find

$$K_1 = \frac{\partial(x, y, z, p_x, p_y, p_z)}{\partial(x', y', p'_x, p'_y, \Theta, \Phi)} = (y'p'_x - x'p'_y)\sin\Theta = J\sin\Theta. \tag{A.6}$$

We can now compute the required Jacobean K quite easily. Because the transfomation from the (x', y', p'_x, p'_y) variables to the action angle variables (θ, θ', J, I) is canonical, it is volume preserving, and we have

$$K_2 = \frac{\partial(x', y', p'_x, p'_y, \Theta, \Phi)}{\partial(\theta, \theta', J, E, \Theta, \Phi)} = \frac{\mathrm{d}I}{\mathrm{d}E}. \tag{A.7}$$

A standard result in classical mechanics shows that $dI/dE = \tau$, where τ is the periodicity of the angle variable θ' which is conjugate to I; for the system we consider that this periodicity is simply the period between between collisions with the walls. Combining (A.4), (A.6) and (A.7) we find

$$K = K_1K_2/J^2\sin\Theta = \tau/J \tag{A.8}$$

as required.

Appendix B

In this appendix we give an alternative derivation of the limiting form of the sum over the resonances (4.23) in the limit where the resonances are dense. We show that the limiting form can be obtained by assuming that successive bounces are uncorrelated. Although this assumption is physically incorrect, it leads to the same result as the limiting integral expression of the type (4.24). The result does not depend on any specific features of the dynamics of a particle bouncing inside a smooth sphere, and could be generalized to other boundaries with integrable dynamics.

Equation (4.2) can be written in general form as

$$\Delta E(\omega, t, \tau) = F(\tau) \sum_{n=0}^{N} \cos(n\omega\tau) \cos[n\phi(\tau)] \tag{B.1}$$

where $F(\tau)$ takes into account the variation of the energy transfer as a function of τ, and the number of bounces is $N = t/\tau$. (The dependence on the variable θ_0, which does not affect the general discussion, has been removed.) The final expression for $\langle \Delta E^2 \rangle$ is obtained by averaging the square of (B.1) over all values of τ:

$$\langle \Delta E^2 \rangle = \int \mathrm{d}\tau \, \Delta E^2(\omega, t, \tau) \Big/ \int \mathrm{d}\tau. \tag{B.2}$$

As in the main text, the sum can readily be obtained as

$$\tfrac{1}{2} \mathrm{Re} \left(\frac{1 - \exp[\mathrm{i}N(\phi - \omega\tau)]}{1 - \exp[\mathrm{i}(\phi - \omega\tau)]} + \frac{1 - \exp[\mathrm{i}N(\phi + \omega\tau)]}{1 - \exp[\mathrm{i}(\phi + \omega\tau)]} \right). \tag{B.3}$$

The first term has resonances when

$$\phi_k^* - \omega\tau = 2k\pi. \tag{B.4}$$

For this term

$$\Delta E^2(\omega, t, \tau) = \frac{F^2(\tau)}{4} \sum_k \frac{\sin^2 N(\phi_k^* - \omega\tau)}{(\phi_k^* - \omega\tau)^2} \simeq \frac{\pi N}{4} F^2(\tau) \sum_k \delta(\phi_k^* - \omega\tau). \tag{B.5}$$

In order to perform the integral in the numerator of (B.2), the sum in (B.5) can be replaced, when the resonances are closely spaced, by a density of resonances $\rho(\tau)$

$$\sum_k \delta(\phi_k^* - \omega\tau) \to \rho(\tau) = \frac{1}{2\pi} |(\omega - \partial\phi/\partial\tau)| \tag{B.6}$$

which is obtained by differentiating the resonance condition (B.4). Including the identical contribution from the second term in (B.3), substituting for N and integrating over all values of τ gives

$$\begin{aligned}
\langle \Delta E^2(t) \rangle &= 2\pi \int \mathrm{d}\tau \, \frac{t}{4\tau} F^2(\tau) \sum_k \delta(\phi_k^* - \omega\tau) \Big/ \int \mathrm{d}\tau \\
&= 2\pi \int \mathrm{d}\tau \, \frac{t}{4\tau} F^2(\tau) \sum_k \frac{\delta(\tau - \tau_k^*)}{|\partial\phi_k^*/\partial\tau - \omega|} \Big/ \int \mathrm{d}\tau \\
&= \frac{\pi}{2} \int \frac{t}{\tau} F^2(\tau) \frac{\rho(\tau)}{|\partial\phi/\partial\tau - \omega|} \Big/ \int \mathrm{d}\tau \\
&= \frac{t}{4} \int \mathrm{d}\tau \, \frac{1}{\tau} F^2(\tau) \Big/ \int \mathrm{d}\tau.
\end{aligned} \tag{B.7}$$

This expression is exactly the same as that which would be obtained from (B.1) and (B.2) under the erroneous assumption that successive bounces are uncorrelated so that

$\langle\cos^2 n\omega\tau\rangle = \langle\cos^2\phi\rangle = \frac{1}{2}$. In this case, squaring (B.1), performing this averaging, and integrating over τ reproduces (B.7) directly.

We illustrate this result by rederiving (4.25) under the assumption that the bounces are uncorrelated: using (4.2) and (4.3) and assuming uncorrelated bounces gives

$$\Delta E^2(\omega, t, \tau) = \frac{t}{\tau}\sin^2\Theta\langle\cos^2\theta_n\rangle\langle\cos^2\omega t_n\rangle\frac{A^2\cos^2\phi}{(\Gamma+\cos^2\phi)^2}$$

$$= \frac{v_F t}{8a}\sin^2\Theta\frac{A^2\cos\phi}{(\Gamma+\cos^2\phi)^2}. \tag{B.8}$$

This expression must be averaged over phase space by integrating over angular momentum as described in detail in section 4. The result is

$$\langle\Delta E(t)^2\rangle = \frac{A^2 t v_F \pi}{3aD}\int \mathrm{d}J\,\mu(J)\frac{\cos\phi}{(\Gamma+\cos^2\phi)^2} \tag{B.9}$$

where $\mu(J) = \tau/J$ and D is the integral (4.14). The integral in (B.9) can be shown to have the value $2m^2a^2v_F F(\Gamma)$, where $F(\Gamma)$ is the function defined in (4.24). Combining (B.9) with (2.6) and (2.8) gives

$$\frac{\mathrm{d}E_T}{\mathrm{d}t} = \frac{4\epsilon_0^2 E_F^2 m^2\omega^2\mathcal{E}_0^2 a^2}{3\pi e^2 n^2\hbar^3}F(\Gamma) \tag{B.10}$$

which is identical to (4.25). Note that the result is obtained much more rapidly under the assumption that the bounces are uncorrelated, and that the derivation only requires that the resonances are dense.

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