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Optical absorption in small metal particles

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Abstract. The optical absorption of small metal particles is investigated using the hard-walled sphere model of non-interacting electrons in an infinitely deep spherical potential well. An analytical formula is obtained for the frequency-dependent dielectric function, valid if the particle radius greatly exceeds the inter-electron spacing. The exact result lies between the earlier approximations of Kawabata and Kubo and of Hache *et al* for the same model. As the radius gets smaller, the absorption shows pronounced oscillations, attributable to shell effects, as a function of frequency.

1. Introduction

The linear and non-linear optical properties of very small metal particles are of current theoretical and experimental interest. There are strong quantum size effects (Perenboom *et al* 1981, Kubo *et al* 1984, Halperin 1986) when the dimensions of the particles are made smaller than the mean free path of electrons in the bulk material. These effects show up, for instance, in the size-dependent broadening of the Mie resonance (Kreibig 1974, Kreibig and Genzel 1985) when the particle size is decreased in the range from about 100 to 10 Å; the resonance width is found to be inversely proportional to the size.

The first quantum mechanical calculation of the width was performed by Kawabata and Kubo (1966). They modelled the metal particle as a system of non-interacting electrons confined inside a hard-walled sphere, i.e. an infinitely deep spherical potential well. The neglect of interactions is a good approximation as long as the particle size is much smaller than the mean free path in the bulk system. The Mie resonance was associated with the excitation of a surface plasma mode; the width results from the decay of this mode into single-particle states. The hard-walled sphere is an idealised model insofar as it ignores band-structure effects, electron–electron interactions and realistic surface potentials. Nevertheless, it is important as the simplest model which captures much of the physics, and has been used recently by Hache *et al* (1986) to estimate non-linear optical susceptibilities of small particles.

However, previous calculations of optical properties using the hard-walled sphere model seem to be in error. The purpose of this paper is to present the correct result for the optical absorption in the model. We derive a closed-form expression valid in the large-size limit, i.e. size far in excess of inter-electron spacing. We also study numerically the deviations from the analytical result when the size is reduced somewhat, and find that the absorption shows oscillatory fluctuations around a smooth background. These oscillations are attributed to shell effects, and we comment briefly on their possible observability in experiment.

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2. The dielectric function

Consider a composite medium consisting of identical, small spherical particles with dielectric constant $\varepsilon \equiv \varepsilon_1 - i\varepsilon_2$ well dispersed in a surrounding medium with dielectric constant ε_0. If the volume fraction of particles is α, the absorption coefficient is given by Mie's formula (Mie 1908)

$$\gamma = \frac{18\pi\alpha\varepsilon_0^{3/2}}{\lambda} \frac{\varepsilon_2}{(2\varepsilon_0 + \varepsilon_1)^2 + \varepsilon_2^2} \tag{1}$$

provided that the wavelength of light $\lambda \gg$ diameter of each particle. The Mie resonance occurs at that frequency $\omega = \omega_R$ at which $2\varepsilon_0 + \varepsilon_1 = 0$. The lineshape is approximately a Lorentzian centred at ω_R, except for very small particles. The linewidth, which shows a systematic dependence on the radius of the particle, is discussed at the end of §2.2.

2.1. Linear response theory

The dielectric constant of the metal particle can be calculated using linear response theory. Since the electrons (each of charge e and mass m) are assumed to be non-interacting, ε_2 can be expressed in terms of the one-electron energies E_i and eigenfunctions $|i\rangle$ (Kawabata and Kubo 1966).

$$\varepsilon_2(\omega) = \frac{4\pi^2\hbar}{\omega^3 V} \sum_{i,j} \frac{f(E_i)(1 - f(E_j))}{E_j - E_i} |\langle j|\dot{J}_z|i\rangle|^2 \delta(\hbar\omega - E_j + E_i). \tag{2}$$

Here V is the volume of the particle, $\dot{J}_z$ is the rate of change of the current operator and $f(E_i)$ is the occupation number of state i, given at temperature T and chemical potential μ by

$$f(E_i) = \frac{1}{\exp[(E_i - \mu)/T] + 1}. \tag{3}$$

In a hard-walled sphere of radius a, each eigenfunction is a product of a spherical harmonic $Y_{lM}(\Omega)$ and the radial eigenfunction

$$R_{nl}(r) = \left(\frac{2}{a^3}\right)^{1/2} \frac{j_l(k_{nl}r)}{j_{l+1}(k_{nl}a)}. \tag{4}$$

Here j_l is the spherical Bessel function of order l and (ak_{nl}) is the location of its nth zero. The corresponding one-electron energy is

$$E_{nl} = \frac{\hbar^2 k_{nl}^2}{2m}. \tag{5}$$

The matrix element which appears in (2) can be evaluated to yield

$$\langle n_1 l_1 M_1|\dot{J}_z|n_2 l_2 M_2\rangle = \frac{e\hbar^2 k_{n_1 l_1} k_{n_2 l_2}}{m^2 a} \delta_{M_1,M_2} \left(C_{l_1}^{M_1}\delta_{l_1,l_2+1} + C_{l_2}^{M_2}\delta_{l_2,l_1+1}\right) \tag{6a}$$

with

$$C_l^M = \left(\frac{l^2 - M^2}{4l^2 - 1}\right)^{1/2} \tag{6b}$$

At $T = 0$, the Fermi function (equation (3)) is replaced by the step function $\theta(\mu - E_i)$. On noting that $\sum_M (C_l^M)^2 = l/3$ and that there are two spin states for each electron, we obtain

$$\varepsilon_2(\omega) = \frac{16\pi e^2}{m^2 a^5 \omega^4} S(\omega) \tag{7}$$

with

$$S(\omega) = \sum_{\substack{n_1 l_1 \\ n_2 l_2}} \tfrac{1}{2}(l_1 \delta_{l_1, l_2+1} + l_2 \delta_{l_2, l_1+1}) E_{n_1 l_1} E_{n_2 l_2} \theta(\mu - E_{n_1 l_1}) \theta(E_{n_2 l_2} - \mu) \delta(\hbar\omega + E_{n_1 l_1} - E_{n_2 l_2}). \tag{8}$$

2.2. *The limit* $k_F a \to \infty$

In the limit $k_F a \to \infty$ where $k_F \equiv (2\mu m/\hbar^2)^{1/2}$ is the Fermi wavevector, the sums over (n_1, l_1) and (n_2, l_2) in (8) for $S(\omega)$ may be replaced by integrals, to yield

$$\tilde{S}(\omega) = \int_0^\infty \mathrm{d}n_1 \, \mathrm{d}l_1 \, \mathrm{d}n_2 \, \mathrm{d}l_2 \, l_1 E_{n_1 l_1} E_{n_2 l_2} \theta(\mu - E_{n_1 l_1}) \theta(E_{n_2 l_2} - \mu) \times \delta(l_1 - l_2) \delta(\hbar\omega + E_{n_1 l_1} - E_{n_2 l_2}). \tag{9}$$

Several authors have obtained (9) or its equivalent, but have not evaluated the integral correctly (Kawabata and Kubo 1966, Ruppin and Yatom 1976, Tran Thoai and Ekardt 1982, Hache *et al* 1986) in the asymptotic limit $k_F a \to \infty$. We use the Debye expansion for large-order Bessel functions (Abramowitz and Stegun 1965). Then ka, the nth zero of the lth-order Bessel function, is given by

$$l + \tfrac{1}{2} = ka \cos\phi \tag{10a}$$

$$\pi(n - \tfrac{1}{4}) = ka(\sin\phi - \phi\cos\phi) \tag{10b}$$

where ϕ runs from 0 to $\pi/2$. The parametrisation is designed for large values of l, but works remarkably well even for low values; for instance, for $l = n = 1$, the error made is less than 1 per cent. An example of the usefulness of (10*a*, *b*) in the large-ka limit is the fact that it yields the correct bulk density of states (Lambert 1968).

$\tilde{S}(\omega)$ can be evaluated in closed form using (10*a*, *b*). Here we present the principal steps. Noting that the Jacobian of the transformation of (10) is $(ka^2/\pi)\sin^2\phi$, we can rewrite $\tilde{S}$ as

$$\tilde{S}(\omega) = \left(\frac{\hbar^2}{2m}\right)^2 \frac{a^4}{\pi^2} \int \mathrm{d}k_1 \, \mathrm{d}k_2 \, k_1^4 k_2^3 \, \theta(k_F - k_1)\theta(k_2 - k_F) \, \delta(\hbar\omega + E_1 - E_2) \, A(k_1, k_2) \tag{11}$$

where $A(k_1, k_2)$ is the 'angular' integral

$$A(k_1, k_2) = \int_0^{\pi/2} \mathrm{d}\phi_1 \, \mathrm{d}\phi_2 \, \cos\phi_1 \sin^2\phi_1 \sin^2\phi_2 \, \delta(k_1 \cos\phi_1 - k_2 \cos\phi_2) \tag{12}$$

Noting that $k_1 \leq k_2$ (as guaranteed by the θ functions in (11)) the integral over ϕ_1 can be performed. Then $A(k_1, k_2)$ involves an integral over the single variable $y \equiv \sin\phi_1$.

$$A(k_1, k_2) = \frac{k_1}{k_2^2} \int_0^1 \mathrm{d}y\, y^2 \left(y^2 + \frac{k_2^2}{k_1^2} - 1 \right)^{1/2}$$
$$= \frac{k_2}{4k_1^2} W(k_1/k_2) \tag{13a}$$

with

$$W(z) = \frac{1}{2} \left[1 + z^2 - \frac{(1-z^2)^2}{2z} \log\left(\frac{1+z}{1-z} \right) \right]. \tag{13b}$$

On substituting equations (13) into (11), the integral over E_2 can be performed, with the result

$$\tilde{S}(\omega) = \frac{\mu}{16\pi^2} (k_F a)^4\, G(v) \tag{14}$$

where $v \equiv \hbar\omega/\mu$ and

$$G(v) = \int_{1-v}^1 \mathrm{d}x\, x^{1/2}(x+v)^{3/2}\, W\left([x/(x+v)]^{1/2}\right). \tag{15}$$

This integral can be performed with the result

$$G(v) = g(v) - g(-v) \tag{16a}$$

where

$$g(v) = \frac{(1+v)^{3/2}}{3} + \frac{v^2(1+v)^{1/2}}{4} - \frac{v^2(2+v)}{8} \log\left| \frac{\sqrt{1+v}+1}{\sqrt{1+v}-1} \right|. \tag{16b}$$

The result for $\varepsilon_2(\omega)$ is finally (as $k_F a \to \infty$)

$$\varepsilon_2(\omega) = \frac{4}{\pi} \frac{e^2}{\hbar\omega a} \frac{1}{v^3} G(v). \tag{17}$$

Our result for $G(v)$ is different from the results $G_{KK}(v)$ and $G_{HRF}(v)$ of Kawabata and Kubo (1966) (KK) and Hache *et al* (1986) (HRF) respectively. KK took the location of the nth zero of the lth-order spherical Bessel function to be at $(l + 2n)\pi/2$. While this is correct if $n \gg l$, a sizable fraction of all states with a given energy have $n \leq l$ and so the KK approximation is not valid. The result of the KK approximation is correctly quoted by Ruppin and Yatom (1976); $G_{KK}(v)$ is $8v/\pi^2$ times the function $g_s(v)$ in their equation (35).

As pointed out by HRF, the KK approximation for Bessel function zeros leads to the incorrect bulk density of states. HRF inserted the correct density of states at one point in their calculation, but their replacement of integrations over $(n_1, l_1), (n_2, l_2)$ by integrations over E_1, E_2 remains approximate. Their result is $G_{HRF}(v) = (\pi^2/6) G_{KK}(v)$.

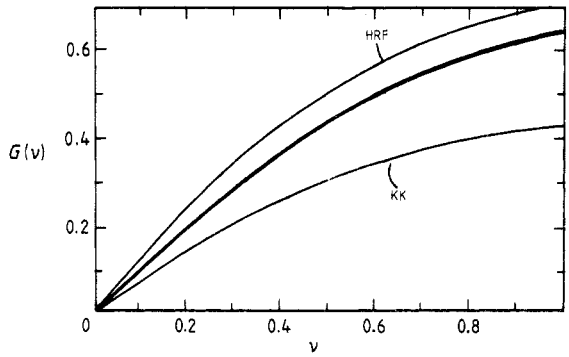

Figure 1. The function $G(v)$ (related to ϵ_2 through (17)) displayed for the hard-walled sphere model. The results of the Kawabata–Kubo (1966) (KK) approximation (as quoted by Ruppin and Yatom 1976) and the approximation of Hache *et al* (1986) (HRF) are also shown for comparison.

Figure 1 displays our result for $G(v)$ (equation (16)), and also for comparison $G_{KK}(v)$ and $G_{HRF}(v)$. The KK approximation underestimates $\varepsilon_2(\omega)$ for all ω whereas the HRF approximation gives an overestimate.

In the limit of large radii, the real part $\varepsilon_1(\omega)$ of the dielectric function is approximately

$$\varepsilon_1(\omega) = 1 - \omega_p^2/\omega^2. \tag{18}$$

Here $\omega_p \equiv (4\pi ne^2/m)^{1/2}$ is the plasma frequency and n is the electron density given by $k_F^3/3\pi^2$. The absorption as a function of frequency is given by equations (1), (17) and (18). The full width Γ at half the maximum of the Mie resonance is given by $2\varepsilon_2/|\partial\varepsilon_1/\partial\omega|$ evaluated at ω_R. The result is

$$\Gamma = \frac{3}{4}\frac{G(v_R)}{v_R}\frac{v_F}{a} \tag{19}$$

where v_F is the Fermi velocity and $v_R \equiv \hbar\omega_R/\mu$. In the limit $v \to 0$, we see from (16) that the ratio $G(v)/v$ approaches unity; the ratio is less than unity for non-zero values of v.

2.3. k_Fa large but finite: shell effects

In the limit $k_Fa \to \infty$, the sum $S(\omega)$ may be replaced by the integral $\tilde{S}(\omega)$. It is also interesting to study the behaviour of $S(\omega)$ when k_Fa is large but finite, taking on values in the experimentally accessible range. To this end, we have performed the sum over states in (8) numerically, using the fact that E_{nl} are determined by the zeros of Bessel functions. Since the result is a sum of delta function peaks in frequency, comparison with the smooth limiting function is most conveniently done by plotting the integrals of the functions. Consequently, we define

$$\tilde{H}(v) \equiv \int_0^v dv'\, G(v') \tag{20}$$

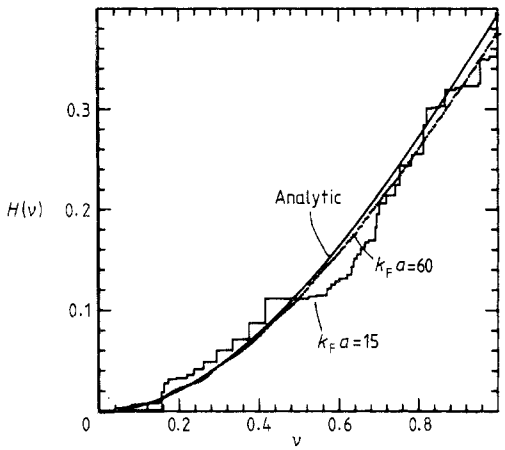

Figure 2. The integral $H(\nu)$ as a function of ν. The analytical result (valid for $k_F a \to \infty$) is shown, along with the results of explicitly performing the sum in (8) for $k_F a = 15$ and 60.

and

$$H(\nu) = \frac{16\pi^2\hbar}{\mu^2}(k_F a)^{-4} \int_0^{\mu\nu/\hbar} d\omega\, S(\omega). \tag{21}$$

We expect that $H(\nu)$ should approach $\tilde{H}(\nu)$ as $k_F a \to \infty$.

Figure 2 shows plots of $\tilde{H}(\nu)$ and of $H(\nu)$ for $k_F a = 15$ and $k_F a = 60$. On the scale of the figure, the curve for $k_F a = 60$ is quite smooth and close to the limiting form $\tilde{H}(\nu)$, incidentally providing a check on our formula for $G(\nu)$ (equation (16)). In contrast, the curve for $k_F a = 15$ has the character of a staircase, with fluctuations on two distinct energy scales. On the smaller scale there are jumps corresponding to individual transitions; but also apparent in the figure are excursions of the entire curve on either side of a smooth background. Very similar oscillatory features are present in the integrated density of states of finite spheres (Balian and Bloch 1972, Subrahmanyam and Barma 1989), where the large-scale fluctuations are recognised to be a consequence of correlations between the single-particle states, as in shell effects in nuclear physics (Bohr and Mottelson 1975). The fluctuations in figure 2 appear to be the optical absorption manifestation of these effects. As in the case of the density of states, both the amplitude and period of the optical absorption fluctuations depend strongly on the size; for larger sizes the fluctuations are more rapid and of smaller amplitude, and quickly become insignificant as shown by the smooth curve obtained for $k_F a = 60$.

3. Conclusion

The principal point of this paper was to present the correct result for $\varepsilon_2(\omega)$ and the plasma resonance linewidth for the hard-walled sphere model in the asymptotic limit $k_F a \to \infty$. As we have seen, the resonance width is inversely proportional to the radius, with a slope which is larger than in the KK approximation but smaller than in the HRF approximation.

There has been some discussion in the literature about the KK result being too small by a factor of about 2 compared with the experimentally determined ε_2 for small silver particles in a glass matrix (Kreibig 1974). There is a smaller discrepancy between the experiment and the correct result (which is approximately 50% larger than the KK result for $v \simeq 0.6$ appropriate for Ag). Given the simplicity of the model, perhaps one should not expect more detailed agreement, especially in view of the fact that the measured width is found to depend strongly on the matrix surrounding the metal particles (Kreibig and Genzel 1985).

Most experiments have been done on particles whose radius is in the range 10 to 100 Å. However, recently there have been some studies of much smaller particles. de Heer *et al* (1987) and Selby *et al* (1989) have studied the Mie resonance in free Na clusters with fewer than 70 atoms. Selby *et al* conclude that the inverse radius dependence of the width breaks down for such small clusters. However, Charlé *et al* (1989) find that width $\sim$ (radius)$^{-1}$ continues to hold for Ag particles in an argon matrix down to radii $\simeq$ 5 Å. But for particles as small as the ones in these experiments, the lineshape deviates significantly from a simple Lorentzian and deserves careful investigation.

Selby *et al* (1989) observe that the plasma resonance in Na clusters is characterised by a single peak for clusters with filled electronic shells, and by a split peak for incompletely filled shells. This shell effect is plausibly attributed to deviations from sphericity away from shell fillings. From the present model we may infer that there is also another source of structure in the lineshape, even for purely spherical particles, if they are small enough. As we see from figure 2, $\varepsilon(\omega)$ exhibits noticeable oscillatory fluctuations around a smooth background as a function of ω. Correspondingly, the lineshape would be expected to develop an oscillatory structure as well. Interestingly, Charlé *et al* (1989) have observed the emergence of a structure in the lineshape when the radius of Ag particles in argon falls below 10 Å. Also, Genzel *et al* (1975) had earlier observed a structure in the lineshape for Ag particles embedded in glass, in a similar range of radii. It would be interesting to investigate the full lineshape for such small particles within the present model.

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References

Abramowitz M and Stegun I A (ed.) 1965 *Handbook of Mathematical Functions* (New York: Dover) p 366
Balian R and Bloch C 1972 *Ann. Phys., NY* **69** 76
Bohr A and Mottelson B R 1975 *Nuclear Structure* vol 2 (Reading, MA: Benjamin) ch 6
Charlé K P, Schulze W and Winter B 1989 *Z. Phys.* D to be published
de Heer W A, Selby K, Kresin V, Masui J, Vollmer M, Châtelain A and Knight W D 1987 *Phys. Rev. Lett.* **59** 1805
Genzel L Martin T P and Kreibig U 1975 *Z. Phys.* B **21** 339
Hache F, Ricard D and Flytzanis C 1986 *J. Opt. Soc. Am.* B **3** 1647
Halperin W P 1986 *Rev. Mod. Phys.* **58** 533

Kawabata A and Kubo R 1966 *J. Phys. Soc. Japan* **21** 1765
Kreibig U 1974 *J. Phys. F: Met. Phys.* **4** 999
Kreibig U and Genzel L 1985 *Surf. Sci.* **156** 678
Kubo R, Kawabata A and Kobayashi S 1984 *Annual Rev. Mater. Sci.* **14** 49
Lambert R H 1968 *Am. J. Phys.* **36** 417
Mie G 1908 *Ann.Phys., Lpz.* **25** 377
Perenboom J A A J, Wyder P and Meier F 1981 *Phys. Rep.* **78C** 173
Ruppin R and Yatom H 1976 *Phys. Status Solidi* b **74** 647
Selby K, Vollmer M, Masui J, Kresin V, de Heer W A and Knight W D 1989 *Phys. Rev.* B submitted
Subrahmanyam V and Barma M 1989 *J. Phys. A: Math. Gen.* **22** L489
Tran Thoai D B and Ekardt W 1982 *Solid State Commun.* 41 687