PHYSICAL REVIEW B VOLUME 36, NUMBER 8 15 SEPTEMBER 1987-I

Wave-vector dispersion versus angular-momentum dispersion of collective modes in small metal particles

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(Received 4 June 1987)

The wave-vector dispersion of collective modes in small particles is investigated within the time-dependent local-density approximation as applied to a self-consistent jellium particle. It is shown that the dispersion of the volume plasmons can be understood from that in an infinite electron gas. For a given multipole an optimum wave vector exists for the quasiresonant excitation of the volume mode but not for the surface mode. It is pointed out that—for the volume modes—the hydrodynamic approximation gives a reasonable first guess for the relation between frequencies and size-quantized wave vectors.

In a recent paper[1] Dozier and Gibbons discuss the wave-vector dispersion of the giant atomic resonances which were found in photoabsorption and photoemission of the rare gases[2] and in other elements.[3] As explicitly shown by Zangwill and Soven[4] these giant resonances can be understood as collective charge-density oscillations of all the electrons of a given atomic shell and have, therefore, much in common with ordinary plasmons in a homogeneous electron liquid.

However, because of the spherical symmetry of the atom, the wave vector is not a conserved quantity but, instead, the angular momentum is a "good" quantum number. For this reason, we have a competition between the shape-enforced "angular-momentum" dispersion (resonance frequencies as a function of l) and the wave-vector dispersion (e.g., measured in an angle-resolved energy-loss experiment) of these modes. If the charge-density oscillations preserve their character as longitudinal excitation modes (as they do at least locally) we would expect to find the multipole-plasmon eigenfrequencies at certain wave vectors on the known dispersion relation of the homogeneous electron gas (as is trivially the case within the local dielectric theory of classical electrodynamics). However, as the results of Dozier and Gibbons show this expectation is wrong and the reason is simply that the atomic shell electrons are, of course, too inhomogeneous.

For small metal particles the situation is slightly different. Compared to an atom, it is a relatively extended object and, as we have already found in our previous study of the optical properties,[5] fairly well-defined volume plasmons do exist for all electron numbers down to $N=20$. The frequencies are a little blue shifted and, in addition, the modes are heavily perturbed by Landau damping.

In a general context, the excitation of these size-quantized volume plasmons is a nonresonant process because the photon does not provide the momentum the plasmon needs. This is just another way of saying that the plasmon is to a considerable extent still a longitudinal mode. It is only because of the nonlocal response that it can be excited by photons. Hence, we expect—in contrast to the surface modes—a more efficient excitation of these modes by inelastic electron scattering. The disadvantage

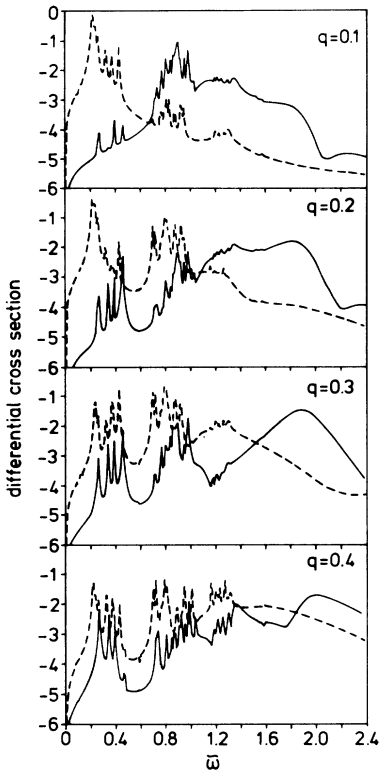

FIG. 1. The $l=1$ part, δ_1, of the differential cross section, Eq. (2), for four different q values $q=0.1$, 0.2, 0.3, and 0.4 inverse Bohr in the LDA (dashed line) and in the TDLDA (continuous line). The example discussed corresponds to a spherical jellium particle with parameters pertaining to 92 valence electrons of Na: $r_s=4a_0$ and $R=18.057a_0$. The value of the energy loss is given in units of the classical surface dipole frequency of a "sodium sphere:" $\tilde{\omega}=E/(\omega_p\sqrt{3})$. Shown is the $\log_{10}$ of the quantity δ_1, Eq. (2), measured in units of R^3. The resonant excitation of the first dipolar volume plasmon around $\tilde{\omega}=1.9$ at $q=0.3$ is clearly resolved. Likewise, the absence of dispersion in the dipolar surface plasmon peak is nicely seen. Similar curves are obtained for the other partial waves $l=0$ to 11. From the frequency shift of the surface peak for different l values the angular-momentum dispersion is obtained.

of this way of exciting plasmons is obvious because we cannot disentangle (experimentally) the various angular momenta. As shown in a recent Letter by Ferrell and Echenique,[6] a rather large number of partial waves is needed to reach convergence in the cross section for inelastic electron scattering by small metal particles. It was exactly for this reason that the theory of inelastic electron scattering by small particles in general was not worked out properly until Ref. 6 was published. Whereas Ref. 6 was based on the classical multipole polarizabilities of a sphere given as

$$\alpha_1^{cl}(\omega) = R^{2l+1}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+(l+1)/l} , \tag{1}$$

where R is the radius of the sphere, $\epsilon(\omega)$ the frequency-dependent local bulk dielectric constant of the solid in question, and l is the polarity of the mode, Ref. 5 was based on a microscopic response model with full inclusion of nonlocal and exchange-correlation-induced quantum effects, respectively. However, in Ref. 5 the evaluation of the exact expression for the differential cross section (in Ry atomic units),

$$\frac{\partial^2\sigma}{\partial E_f \partial \Omega_{k_f}} = 8\frac{k_f}{k_i}\frac{1}{\pi}\frac{1}{q^4}\sum_{l=0}^{\infty} 4\pi(2l+1)\int_0^\infty dr\, r^2 j_l(qr)\int_0^\infty dr'(r')^2 j_l(qr')\mathrm{Im}\chi_l(r,r';\omega_{if})$$
$$\equiv \frac{4}{\pi}\frac{k_f}{k_i}\frac{1}{q^4}\sum_{l=0}^{\infty}\delta_l \equiv \frac{4}{\pi}\frac{k_f}{k_i}\frac{1}{q^4}\delta , \tag{2}$$

was restricted to relatively small wave vectors q. In Eq. (2), χ_l is the lth component of the retarded density-density correlation function, ω_{if} and q are the transferred energy and momentum. j_l are the spherical Bessel functions, and Im means the imaginary part. To answer the questions discussed above, we need to calculate the full expression of Eq. (2), which is a formidable task. The interesting results of this study are communicated in the present work. For the discussion to follow the prefactor of Eq. (2) is unimportant. Hence this discussion is based on the sum over δ_l.

To begin, Fig. 1 shows the $l=1$ part, δ_1, of the total quantity δ under discussion for wave-vector transfers $q=0.1$, 0.2, 0.3, and 0.4 inverse Bohr. This figure should be compared to the optical excitation spectrum which was discussed in length in Refs. 7–9. To facilitate the discussion of the collective features in these curves we give as a dashed line the independent electron result, calculated within the LDA. That means in the calculation of Eq. (2) χ_l^0 is used instead of χ_l. The continuous line in the figure is the TDLDA. Because we discussed already in Refs. 7–9 how to identify a certain feature in these curves as being a collective one, this discussion is not repeated here, but in Fig. 2 the optical spectrum is given again where the collective modes are characterized by an arrow. The mode around 0.9 is the dipolar surface plasmon and the broad hump around 1.9 is the optically excited first dipolar volume plasmon. Note that the surface plasmon has a rather small damping, whereas the volume mode is heavily damped. Both features were discussed at length in a previous work and the discussion is, therefore, not reproduced here. For comparison, the classical spectrum is given as a chain line. The optical excitation of the volume plasmon is missing in the classical spectrum, simply because of the local character of the classical theory.

On comparing the optical spectrum with the loss spectrum at various wave vectors we see clearly how the volume plasmon excitation is turned on and at the same time the surface plasmon excitation is turned off. Whereas in the optical spectrum the red-shifted Mie resonance is the dominating feature, it is increasingly the volume plasmon in the loss spectrum. At a wave vector of $q=0.3$ the $l=1$ volume plasmon is obviously resonantly excited. At this wave vector, the surface mode does not carry much oscillator strength but is still clearly resolved. Hence we see to which extent the surface plasmon is transverse in character and to which extent the volume plasmon is a longitudinal excitation. Similar curves were obtained for the other angular momenta ($l=0$ to 11) with basically the same results. The collective modes, already identified in the optical polarizabilities,[9] are dramatically enhanced in the energy-loss matrix element which means nothing else than that "the multipole plasmon needs more momentum transfer than the photon can provide." For the example under study, the volume plasmon can be clearly resolved up to $l=5$. On the other hand, on comparing the dashed curves with the continuous ones we see

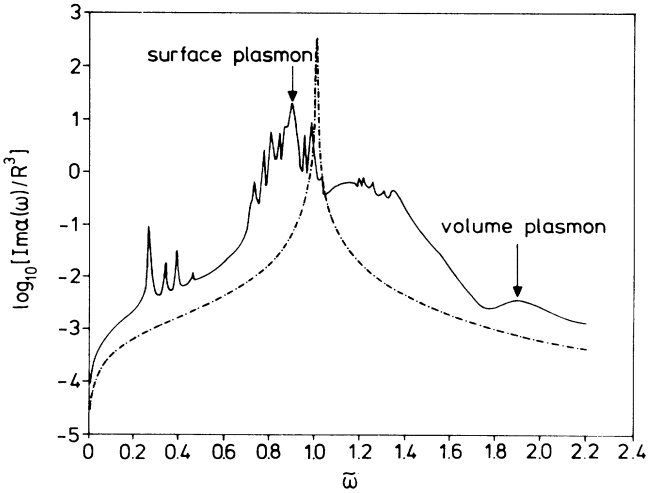

FIG. 2. Imaginary part of the dynamical polarizability, in units of R^3, for the same particle as discussed in Fig. 1. The continuous line is the TDLDA result, the chain line is the classical Drude result. This figure was discussed at length, especially in Ref. 8. In order to facilitate the comparison with the energy-loss spectrum, it is reproduced here. The collective modes are characterized by an arrow. The sharp line around 0.9 is the dipolar surface plasmon and the broad hump around 1.9 is the first dipolar volume plasmon.

that around $q=0.5$ collective features disappear. As already discussed in our previous work[9] this is to be expected because of the existence of the critical wave vector in the bulk (!) and its "partial transferability" to finite-size objects.

Before continuing we want to comment about the q dependence of the excitation spectrum in the volume plasmon region of the various l channels. For low-l values ($l=0$, 1, 2, 3) we find the following q values for the most efficient excitation at the lowest volume mode of each l: $q=0.25$, 0.3, 0.35, and 0.4. All the modes are relatively broad as revealed in Fig. 1 for $l=1$. It is interesting, now, to compare these q values with the corresponding result of the hydrodynamic theory, published in Ref. 10, because for the volume modes (and in sharp contrast to the surface modes) the hydrodynamic approximation can be expected to give a reasonable first approximation to the microscopic response equations. Within hydrodynamic theory, the allowed q values for a mode of type l in a sphere of radius R are approximately given[10] by the zeros of the spherical Bessel function $j_{l+1}(qR)=0$. This condition yields for the first allowed q value and the four values $l=0$ to 3 the numbers: $q=0.21$, 0.28, 0.35, and 0.42 which are in surprisingly good agreement with those obtained from the microscopic theory (see above). Of course, hydrodynamic theory does not tell us anything about the damping, which is intrinsically beyond the scope of this approximation.

The difficulty in an energy-loss experiment with fast electrons is that none of the structures discussed in Fig. 1 is directly accessible experimentally, because in the total quantity, Eq. (2), all l channels contribute! For the example under discussion, a jellium particle corresponding to 92 valence electrons of Na, 12 partial waves have to be taken into account to make the total cross section convergent for q values smaller than one inverse Bohr (which means a considerable amount of computer time). Typical results are shown in Fig. 3 for a relatively small-q value (0.1), for an intermediate one (0.3), and, finally, for a large q value (0.9) where collective behavior does not play any role.

Analyzing carefully the results shown in the figures, we find that the various l-channel surface plasmons (one per l value) have nearly no q dispersion.[11] This is especially clear in Fig. 1 where the Mie peak stays nearly constant at 0.9 both in the optical spectrum and in the loss spectrum (as long as it can be identified). The same is true for other l channels not shown in the figures. The most pronounced feature with the surface plasmons is their q-dependent oscillator strength. As a consequence, all the various surface plasmons show up in an energy-loss experiment at the same time if the wave vector is sufficiently small. Because there is nearly no q dispersion in the surface peaks[11] we speak instead of the l dispersion of *the* [one (!)] collective surface excitation, which is shown in Fig. 4. In this figure we have assigned each surface mode l an equivalent wave vector q_l via $q_l=l/R$ (Ref. 10). The situation is different for the volume plasmons. The various l channel volume plasmons are superposed in the loss spectrum to give one (or more) broad peak which shows a clear q dispersion ! The dispersion relation we find is given in Fig. 4. The most striking result is that the form

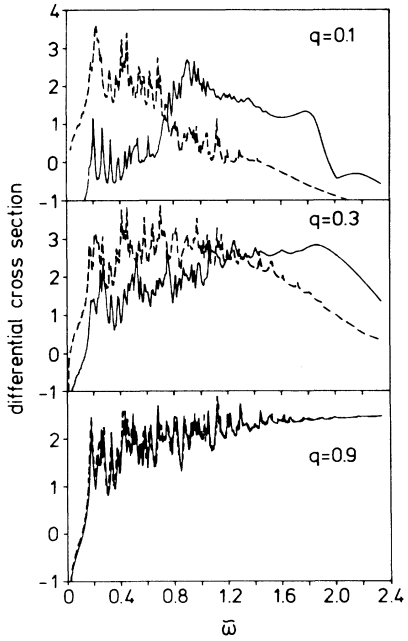

FIG. 3. The total differential cross section δ, Eq. (2), for three different wave vectors $q=0.1$, 0.3, and 0.9. Eleven l values had to be taken into account to obtain convergence for wave vectors smaller than 1. The vanishing of the collective effects at large wave vectors is clearly demonstrated. From the q dispersion of the volume peak we obtain the results shown in Fig. 3.

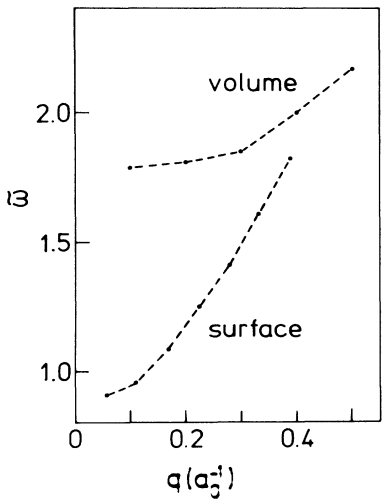

FIG. 4. Angular-momentum dispersion of the surface peak and the wave-vector dispersion of the first volume peak. Each surface mode has been given an equivalent wave vector q_l via $q_l=l/R$. Each dispersion relation shows a square dependence on the wave vector in the low-q limit. However, the dispersion coefficients are *different* for the two modes. If the frequency of the volume mode were shown as a function of q^2 we would obtain a curve which looks very similar to those discussed in Ref. 11. Note that the dispersion of the volume mode is a measurable quantity, whereas the angular-momentum dispersion of the surface mode is not. The latter gives just the calculated frequencies of the various collective surface peaks at their calculated equivalent wave vectors.

of the dispersion curve is nearly identical with those discussed by Gupta, Aravind, and Singwi[12] in a study of the density-density correlation function of a homogeneous electron gas beyond the RPA level.

It is now in order to comment about how to detect experimentally the effects discussed in this paper. Optical experiments on clusters in a beam are now possible in various laboratories, e.g.,[13] but energy-loss experiments are still in a very preliminary stage. Hence, it is tempting to do the experiments on embedded clusters in very much the same way as the rare-gas bubbles in Al were studied by electron-energy-loss spectroscopy.[14] Because of the interaction between the host and the surface of the particle, frequency changes of the surface plasmons *are* to be expected. But all the qualitative findings should be experimentally accessible. These are first, a very weak q dispersion of a given l-pole surface mode; second, a nearly constant oscillator strength for the excitation of these modes up to a certain q value beyond which the excitation quickly drops down; third, the nonclassical l dispersion of the surface modes; fourth, the quasiresonant q excitation of the volume modes and, finally, the q dispersion of the volume mode which should be in near agreement with what is known for an infinite free-electronlike system. Hence, all alkali metals are the principal candidates for experiments to be done in the future.

It is a pleasure to thank Professor E. Zeitler for continuing interest and support. I am grateful to R. Fuchs for critically reading the manuscript and for constructive remarks. Many thanks are due to J. Fink and A. vom Felde for informative discussions on the experimental aspects of the problems investigated.

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