Excited states in metal voids

Raphael de Haro, Jr.* and João da Providência, Jr.
Departamento de Física, Universidade de Coimbra, P-3000 Coimbra, Portugal

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Based on a variational model, we obtain the spectra of excited states in metallic voids. Void plasmons are seen to have a peculiar behavior, concerning the radius of the cavity, which can be ascribed to a delay in the onset of collectivity. This is further demonstrated by the electronic currents and transition densities obtained. One of the major features of the developed method is that it enables us to describe arbitrarily large voids, up to the bulk limit. [S0163-1829(96)08631-6]

INTRODUCTION

Microcavities in metals and in other materials have been the object of much experimental and theoretical activity in the last 30 years. One of the driving reasons for such an interest is the understanding of the processes (damage) occurring in metals by the incidence of neutrons and ions. Cavities are usually filled with some noble gas, especially helium. The presence of such bubbles, even at very low concentrations, causes drastic changes in the metal properties. Among the facilities that lead to a growth of helium bubbles on the constituent, or shielding material, are fast fission and fast breeder reactors, fusion devices, tritium storages, spallation sources, and direct α implantation.[1–3]

In this work we study the collective excitations of voids in metals, originated by the interaction of photons and electrons with the bubbles. Although the large majority of experimental work concerns the structure and formation of bubbles, in the last two decades, many of them also aimed to study the excitation of surface plasmons on voids,[4–11] using, basically, ultraviolet and energy-loss spectroscopy. The gas pressure inside the bubbles varies largely with the bubble size, decreasing with increasing radii.

In our model we will consider spherical voids, with a zero gas concentration inside. Although this situation should be considered as a limiting case of the available experimental data, it turns out to be a good approximation.

Existing theoretical models range from the earlier, purely classical models,[12–16] to more recent works, using density functional theory in a local density approximation,[17] a hydrodynamical approach,[18] and a sum-rule-based method.[19] However, there are still many aspects to be understood concerning the void plasmons.

The present model, based on a variational scheme originally due to Andō and Nishizaki,[20] further developed by da Providência and others[21] and recently successfully applied to the study of clusters,[22] aims to bring a deeper insight into the dynamics of the excited states in cavities, by exploiting the power of the model to obtain not only sum rules and their exhausted fractions, but also transition densities and electronic currents for the excited states.

Since the details of the formalism have already been presented in a previous paper[22] we shall only briefly summarize the main steps in Sec. II, pointing out the changes in the formalism relative to this former work. In Sec. III we collect our results. In Sec. IV, comparison to data is presented and some conclusions are drawn.

THE MODEL

Our physical model is an electron gas in a uniform positive background, the so-called jellium model, which can be summarized by the following Hamiltonian:

$$H=\sum_{j}\frac{p_j^2}{2m}+\sum_{i<j}\frac{e^2}{|\mathbf{x}_i-\mathbf{x}_j|}+\sum_{j}U(\mathbf{x}_j)+W, \tag{1}$$

where the first term is the kinetic energy, $U(\mathbf{x})$ is the potential energy due to the uniform positive density distribution, and W is the electrostatic energy of the positive background ($-e$ being the electron charge).

We assume that the equilibrium electron density is the same as for the jellium described by $n_0(\mathbf{x})=n_0\Theta(r-R)$. We assume that the electron dynamics is well approximated by the Vlasov equation.[21] Since Vlasov dynamics neglects exchange effects and electron-electron correlations, these effects are taken into account phenomenologically by adding a two-body δ interaction (simulating exchange effects) and a three-body δ interaction (simulating correlation effects) to the Hamiltonian. We also add a one-body δ interaction, which describes the effect of the more conventional pseudopotential. The effective energy functional referring to the metal cluster may therefore be expressed as follows:

$$\begin{aligned}E=&\int d\Gamma f\left(\frac{p^2}{2m}+a_1\right)+\frac{1}{2}\int d\Gamma_1\int d\Gamma_2 v_{12}f(1)f(2)\\&+\frac{1}{3!}\int d\Gamma_1\int d\Gamma_2\int d\Gamma_3 v_{123}f(1)f(2)f(3)\\&+E^{(e)}_{e-j}+W.\end{aligned} \tag{2}$$

The inclusion of the effective one-body, two-body, and three-body interactions is essential to confer predictive power to our method. The term $E^{(c)}_{e-j}$ stands for the energy associated with the Coulomb interaction electron-jellium,

$$E^{(c)}_{e-j}=-e^2\int d^3x_1\int d^3x_2\,\frac{n(1)n_0(2)}{|\mathbf{x}_1-\mathbf{x}_2|}, \tag{3}$$

and W stands for the interaction of the jellium with itself:

$$W=\frac{e^2}{2}\int d^3x_1\int d^3x_2\,\frac{n_0(1)n_0(2)}{|\mathbf{x}_1-\mathbf{x}_2|}. \tag{4}$$

In Eq. (2), the term in v_{12} includes the energy associated with the electron-electron Coulomb interaction, $E^{(c)}_{e-e}$,

$$E^{(c)}_{e-e}=\frac{e^2}{2}\int d^3x_1\int d^3x_2\,\frac{n(1)n(2)}{|\mathbf{x}_1-\mathbf{x}_2|}. \tag{5}$$

The symbol f stands for the distribution function of the valence electrons, n is the density of the valence electrons, $d\Gamma=gd^3xd^3p/(2\pi\hbar)^3$ is the volume element in phase space, and $g=2$ the spin multiplicity. The one-, two-, and three-body δ interactions lead to an effective potential energy of the form

$$V_{\text{eff}}=\int d^3x\sum_{\sigma=1}^{3}a_\sigma n^\sigma, \tag{6}$$

where a_σ are force constants adjusted so that we obtain the experimental values of the volume energy, bulk modulus, and density of the metal.

The total energy in the equilibrium state is given by $E=\Omega(\tau+\Sigma_{\sigma=1}^3 a_\sigma n^\sigma)$, where $\Omega=N/n$ stands for the volume of the metal and τ is the kinetic energy density:

$$\tau=g\int\frac{d^3p}{(2\pi\hbar)^3}\,f\,\frac{p^2}{2m}=\frac{4\pi}{(2\pi\hbar)^3}\,\frac{p_F^5}{5m}. \tag{7}$$

The equilibrium distribution function of the valence electron gas is

$$f(\mathbf{x},\mathbf{p})=\Theta\left(\lambda-\frac{p^2}{2m}-U\right)\Theta(R-r), \tag{8}$$

and

$$U=\sum_{\sigma=1}^{3}a_\sigma\sigma n^{\sigma-1} \tag{9}$$

is the self-consistent potential.

The minimum of the total energy yields the equilibrium density and leads to the equilibrium condition:

$$\frac{2\tau_0}{3}+\sum_\sigma a_\sigma(\sigma-1)n_0^\sigma=0. \tag{10}$$

A nonequilibrium state is obtained from the ground state $|\phi_0\rangle$ through

$$|\phi\rangle=\exp\left(\frac{i}{\hbar}\,\hat{S}\right)|\phi_0\rangle, \tag{11}$$

where $\hat{S}$ is a hermitian one-body operator and the dynamics is described (up to second order) by the Lagrangian

$$L^{(2)}=\frac{i}{2\hbar}\langle\phi_0|[\hat{S},\dot{\hat{S}}]|\phi_0\rangle-\frac{2}{2\hbar^2}\langle\phi_0|[\hat{S},[H,\hat{S}]]|\phi_0\rangle. \tag{12}$$

Considering an expansion of $\hat{S}$ in powers of the momentum, restricted to the first two terms,

$$\hat{S}=\sum_{j=1}^{N}\left[\chi(\mathbf{x},t)+\frac{1}{2}\,[\mathbf{p}\cdot\mathbf{s}(\mathbf{x},t)+\mathbf{s}(\mathbf{x},t)\cdot\mathbf{p}]\right], \tag{13}$$

where χ and $\mathbf{s}$ are taken as basic dynamical variables, the Lagrangian reads

$$L^{(2)}=\int d^3x\left\{\frac{n_0}{2}\,(\mathbf{s}\cdot\boldsymbol{\nabla}\dot{\chi}-\dot{\mathbf{s}}\cdot\boldsymbol{\nabla}\chi)\cdot\frac{n_0}{2m}\,(\boldsymbol{\nabla}\chi)\cdot(\boldsymbol{\nabla}\chi)-\frac{\tau_0}{3}\left((\boldsymbol{\nabla}\cdot\mathbf{s})^2+\frac{1}{2}\,(\partial_\alpha s_\beta+\partial_\beta s_\alpha)^2\right)-\sum_\sigma a_\sigma\,\frac{\sigma(\sigma-1)}{2}\,n_0^\sigma(\boldsymbol{\nabla}\cdot\mathbf{s})^2\right.$$
$$\left.-\frac{e^2}{2}\int d^3x_1d^3x_2\,\frac{[\boldsymbol{\nabla}\cdot(n_0\mathbf{s})]_1[\boldsymbol{\nabla}\cdot(n_0\mathbf{s})]_2}{|\mathbf{x}_1-\mathbf{x}_2|}\right\}. \tag{14}$$

We expand the dynamical variables χ and $\mathbf{s}$ in multipoles and their radial dependence in powers of (r/R),

$$\mathbf{s}=\boldsymbol{\nabla}\left(\sum_{k=k_{\min}}^{k_{\max}}b_k(t)(r/R)^kY_{l0}\right), \tag{15}$$

$$\chi=\sum_{k=k_{\min}}^{k_{\max}}a_k(t)(r/R)^kY_{l0}. \tag{16}$$

Requiring the action to be stationary, we obtain the following matrix equation for the variables b_k:

$$-m\sum_k A_{qk}\ddot{b}_k=\sum_k B_{qk}b_k, \tag{17}$$

where we have used one of the equations of motion to eliminate the variable $a_k(t)$.

In the present calculations we choose $k_{\max}=-2$ so that the integrals implied by the Lagrangian (14) do not diverge. According to the choice of $k_{\min}$ we obtain a variational scheme of order $n_{\text{dim}}=k_{\max}-k_{\min}+1$ with n_{dim} eigenmodes.

The matrices A_{kq} and B_{kq} read

$$A_{kq}=-{}_{0}(0)R\,\frac{kq+l(l+1)}{k+q+1} \tag{18}$$

and

$$B_{kq}=\frac{-2}{(k+q-1)R}\left\{\frac{2\tau_0(0)}{3}\{kq(kq-k-q+3)+l(l+1)(2kq-3k-3q+1)+[l(l+1)]^2\}+\left(\frac{\mathcal{B}}{2}-\frac{2\tau_0(0)}{9}\right)[k(k+1)-l(l+1)][q(q+1)-l(l+1)]\right\}+\frac{n_0(0)m\omega_p^2R}{2l+1}\left\{-kq-(k+q)(l+1)+\left[\frac{1}{(q+l+1)(k-l)}+\frac{1}{(k+l+1)(q-l)}-\frac{1}{k+q+1}\left(\frac{1}{q+l+1}+\frac{1}{k+l+1}\right)\right][k(k+1)-l(l+1)][q(q+1)-l(l+1)]\right\}, \tag{19}$$

where

$$\omega_p^2=\frac{4\pi n_0(0)e^2}{m}, \tag{20}$$

is the plasma frequency, or bulk volume plasmon, and $\mathcal{B}$ is the compression modulus.

Solving this system, we obtain a set of eigenvalues, corresponding to the energy spectrum of the excited states and a set of eigenvectors describing the dynamical variables χ (a velocity potential) and $\mathbf{s}$ [$\boldsymbol{\nabla}\cdot(n_0\mathbf{s})$ is the transition density]. These normal modes are orthogonal and it can be shown that they satisfy the single and triple energy weighted sum rules (m_1 and m_3), when we consider an external operator of the form

$$D(\mathbf{x})=\sum_{k=k_{\min}}^{k_{\max}}\nu_k r^k Y_{l0}\,. \tag{21}$$

If we choose $D(\mathbf{x})=r^{-2}$ for $l=0$ and $D(\mathbf{x})=r^{-l-1}Y_{l0}$ for $l>0$, the sum rules read, for $l=0$,

$$m_1=\frac{8\pi n_0(0)}{3mR^3} \tag{22}$$

and

$$m_3=\frac{8\pi}{5m^2R^5}\left(\mathcal{B}+\frac{128}{9}\,\tau_0\right)+\frac{8\pi n_0(0)}{3mR^3}\,\omega_p^2, \tag{23}$$

and, for $l>0$,

$$m_1=\frac{n_0(0)(l+1)}{2mR^{2l+1}}, \tag{24}$$

$$m_3=\frac{2\tau_0(0)}{3m^2R^{2l+3}}\,(l+1)(l+2)(2l+1)+\frac{n_0(0)\omega_p^2(l+1)^2}{2(2l+1)mR^{2l+1}}. \tag{25}$$

It is instructive to write down the ratio of the m_3 to the m_1 sum rules. The result is the energy of the collective mode, provided it exhausts 100% of the sum rules. This quantity, usually called E_3^2, is the energy of the mode that can be obtained in a sum rule approach. For $l=0$,

$$\frac{m_3}{m_1}=\frac{3}{5mn_0(0)R^2}\left(\frac{128}{9}\,\tau_0+\mathcal{B}\right)+\omega_p^2, \tag{26}$$

and for $l>0$ we obtain

$$\frac{m_3}{m_1}=\frac{4}{3mR^2}\,\frac{\tau_0(0)}{\rho_0(0)}\,(l+2)(2l+1)+\frac{l+1}{2l+1}\,\omega_p^2. \tag{27}$$

For $l=0$, one sees that, for increasing radii, the energy approaches the volume plasmon value, $\hbar\omega_p$. The first term, important for smaller radii, depends, basically, as expected, on $n_0(0)$, $\mathcal{B}$, and, implicitly, through the force constants a_σ, in the bulk energy. The formalism describes the dependence of the monopole energy (breathing mode) on the compressibility of the metal, through the bulk modulus $\mathcal{B}$.

For $l>0$, E_3 for large radii converges to $\hbar\omega_p\sqrt{(l+1)/(2l+1)}$, which is the classically obtained energy for void excitations, analogous to the Mie limit for clusters.[12,13,22] The first term depends essentially on the density $n_0(0)$ and on the number of the missing atoms, since $\tau_0(0)/n_0(0)$ is the kinetic energy per valence electron.

NUMERICAL RESULTS

With the choice given before for the excitation operator, we calculate the excitation spectra in some metals. In Fig. 1, we show the excitation of voids in aluminum, as a function of the number of missing atoms in the cavity up to 100, for the first five angular momenta and for several normal modes of each multipolarity. The monopole, already for very few missing atoms, reaches its limiting value, the bulk plasmon $\hbar\omega_p$. The dipole and also the higher multipoles show a blueshift with decreasing radii, in agreement with experimental data.[9] For $l=1,2,\ldots$, surface plasmons are predicted. As a function of the number of missing atoms, the volume plasmons are crossed by the surface plasmons, which are described by much steeper curves. At the crossings, the residual behavior is present and the curves actually behave as if the two modes repelled each other. Available data refer to gas filled bubbles and a direct comparison is subject to restrictions, as already pointed out by other authors.[6,9,17–19] Data are connected to a certain mean bubble radius, in a distribution that is typically some Å wide and the gas density (inside the bubbles) is dependent on the bubble radius.[8] Both factors affect the experimental plasmon energies relative to

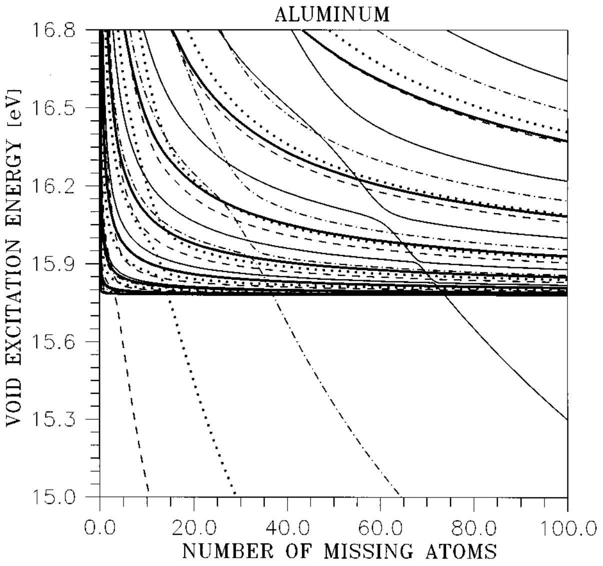

FIG. 1. Excitation spectra of voids in aluminum, as a function of the number of missing atoms in the cavity for the lowest normal modes of the first five angular momenta. The thick full curves refer to $l=0$ normal modes, the dashed curves refer to $l=1$ normal modes, the dotted curves refer to $l=2$ normal modes, the dashed-dotted curves refer to $l=3$ normal modes, and the thin full curves refer to $l=4$ normal modes.

the value expected for a single void.

We may compare for instance, the result of Manzke, Crecelius, and Fink[9] for low He concentration (3.3 at. %) for the $l=1$ mode, $E^{\mathrm{exp}}_{l=1}=11.5$ eV, with our result $E_{l=1}=13.3$ eV. Existing theories systematically overshoot the plasmon energies and the reasons for that have been discussed in the previous works already quoted. The general agreement is good, with a typical discrepancy of 2–3 eV.

An interesting point we want to address is the qualitative difference between the behavior of the plasmon energies for clusters and for cavities, as a function of the number of missing atoms.

For clusters, one sees from Fig. 2 of Ref. 22, that the energies show, for every multipolarity, a smooth decreasing behavior with increasing radii. For voids one has an essentially different behavior: energies show a plateau, whose extent depends on the considered multipolarity (and, as we shall see in the following, also depends on the specific metal).

Figure 2 shows the dipole sum rule exhaustion for 18 eigenmodes in aluminum (ordered in energies from the lowest, $i=1$, to the highest, $i=n_{\mathrm{dim}}$) up to a number of missing atoms well below the end of the plateau that one observes in Fig. 1. The eigenmodes were obtained in a variational calculation where in each of the expansions in Eqs. (15) and (16) we take 18 terms ($n_{\mathrm{dim}}=18$). One sees that below a certain radius (around 10 missing atoms), the lowest mode, which is also expected to be the most collective, bears no collectivity, for it exhausts only a negligible fraction of the total sum rule strength. The other (higher) modes exhaust, for different radii, different shares of the oscillator strength. In Fig. 3, we show the calculated transition densities for the lowest quadrupole mode and for the values of N where a steeper increase of the exhaustion of the energy weighted sum rule takes place. It ranges from the value just below ($N=10$), to a value just above ($N=15$), the end of the plateau, as one can see from Fig. 1. For $N=10$, the transition density $\delta\rho$, characteristically wiggly, shows no collectivity. Through $N=10$–15, the picture changes rapidly, with the smoothening of the curve, ending, for $N=15$, in a transition density that is already characteristic for a collective surface mode (peaked at the surface). This sharp onset of collectivity happens for every multipolarity. The existence of a ''minimum radius'' for having a collective state has already been pointed out by Barberán and Bausells,[18] based on an approximate expres-

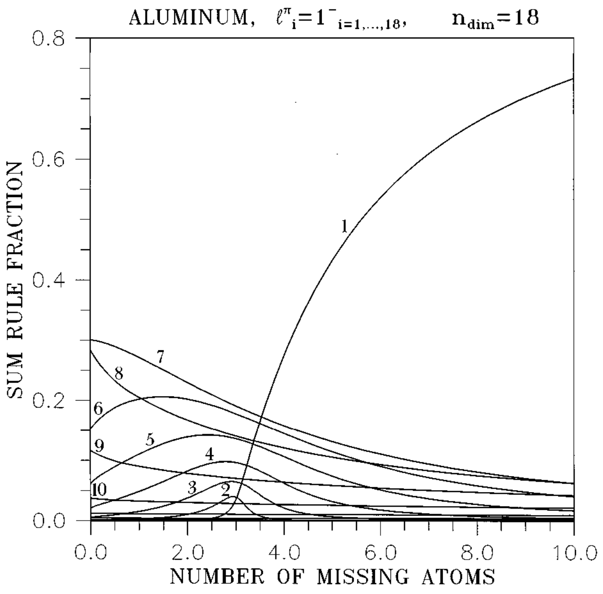

FIG. 2. Dipole sum rule exhaustion for the eigenmodes in aluminum (we have ordered the states from the lowest to the highest energy), as a function of the number of the missing atoms in the cavity.

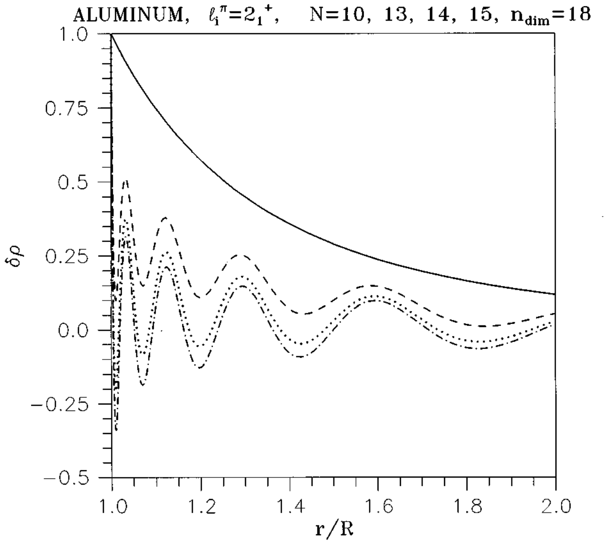

FIG. 3. Transition densities in aluminum, for the quadrupole, for 10, 13, 14, and 15 missing atoms. We have normalized the transition densities to 1 at $r=R$. The full curve refers to $N=15$, the dashed curve refers to $N=14$, the dotted curve refers to $N=13$, and the dashed-dotted curve refers to $N=10$.

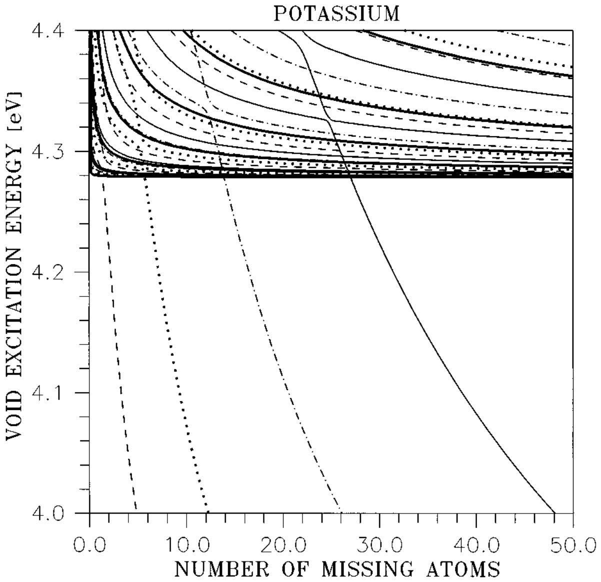

FIG. 4. Excitation spectra of voids in potassium, as a function of the number of missing atoms in the cavity for the lowest normal modes of the first five angular momenta. The thick full curves refer to $l=0$ normal modes, the dashed curves refer to $l=1$ normal modes, the dotted curves refer to $l=2$ normal modes, the dashed-dotted curves refer to $l=3$ normal modes, and the thin full curves refer to $l=4$ normal modes.

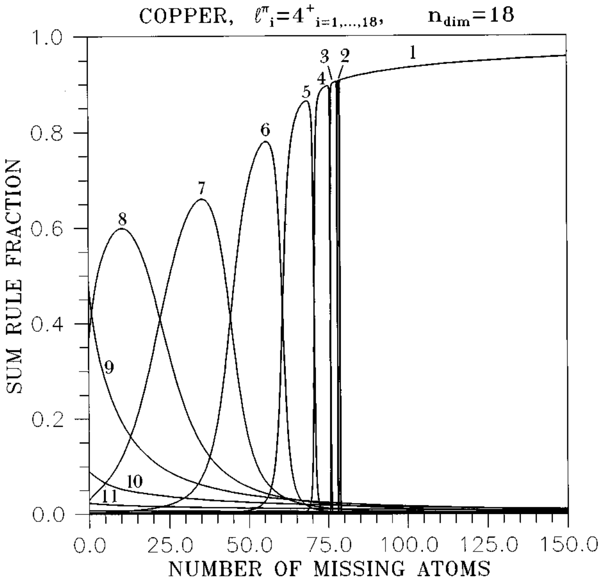

FIG. 5. Hexadecapole sum rule exhaustion for the eigenmodes in copper, as a function of the number of the missing atoms in the cavity. We have ordered the states from the lowest to the highest energy.

sion for the radius obtained analytically. However, they foresee such an effect not only for cavities but also for clusters. According to our calculations[22] this only happens for cavities. Moreover, in our formalism, we can ascribe this lack in collectivity in the lowest eigenmode ($i=1$) to the higher eigenmodes of the system. This effect is strongly dependent on the density and bulk modulus of the metal. So, concerning cavities, we can loosely speak of ''soft'' metals, such as cesium and potassium, where the minimum radius able to sustain a collective mode does not correspond to more than some missing atoms (~1 Å) even for higher multipolarities, as can be seen from Fig. 4. In an analogous way we can speak of ''hard'' metals, such as aluminum and copper, where the minimum radius can correspond to some hundreds of missing atoms (~tens of Å) for higher multipoles, and some tenths for the dipole. In Figs. 5 and 6, we show, respectively, the fraction of the exhausted sum rule and the energy spectrum with the number of missing atoms for the hexadecapole in copper. Since the higher the multipolarity, the more sudden the onset of the collectivity for the lowest eigenmode, we discuss the $l=4$ case. In this case, for up to about 80 missing atoms, there is no collectivity in the $i=1$ mode (i orders the eigenmodes for each multipolarity with increasing order of energy). Note that as long as one does not have any single collective mode exhausting (almost) all the sum rule strength, sum rule based methods loose any predictive power, since this is an ''*a priori*'' hypothesis of such methods. To study whether the higher modes that share fractions of the sum rule strength for some radial interval are indeed collective, we show, in Fig. 7, the transition density and currents for the third ($i=3$) hexadecapole, for $N=78$, where it peaks in the sum rule exhaustion, reaching about 90% of the total strength. The behavior of the transition density, and also that of the currents, in Fig. 7 shows this mode to be a collective surface state.

It is interesting to notice that there is some experimental evidences for plasmons of higher multipolarities, even for small bubbles.[6,7] According to our results, we could suggest that, for those small bubbles, the observed plasmons could correspond to higher eigenmodes, instead of the lowest one.

Concerning to the monopole, Fig. 8 shows the obtained

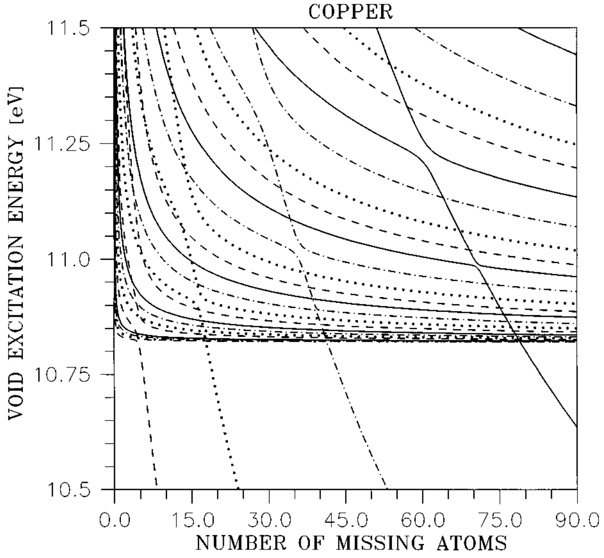

FIG. 6. Excitation spectra of voids in copper, as a function of the number of missing atoms in the cavity for the lowest normal modes of the first five angular momenta. The thick full curves refer to $l=0$ normal modes, the dashed curves refer to $l=1$ normal modes, the dotted curves refer to $l=2$ normal modes, the dashed-dotted curves refer to $l=3$ normal modes, and the thin full curves refer to $l=4$ normal modes.

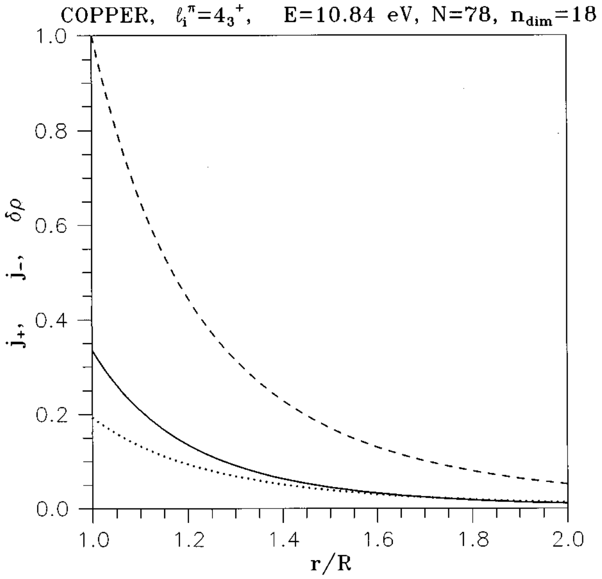

FIG. 7. Transition density and currents for the third hexadecapole, for 78 missing atoms. Currents are presented in terms of radial function $j_\pm$ defined by $j(x)=j_+(r)Y_{ll+10}+j_-(r)Y_{ll-10}$, where $Y_{ll\pm10}$ stands for the vector spherical harmonics. The dashed line refer to j_+ and the dotted curve refers to j_-. The full curve refers to the radial function $-j_{\mathrm{div}}(r)$ defined by the equation $\nabla\cdot j=j_{\mathrm{div}}\mathrm{Y}_{10}$.

sum rule exhaustion. We recall that this result is connected with the choice made for the external operator. In this work, $D(\mathbf{x})=r^{-2}$. Figure 8 shows that no mode bears a sizable fraction of the total strength, which is scattered among the different modes. It must be noted that, with this simple intuitive form of operator, sum rule methods give no reasonable result. In such a case, an adequate procedure is to use the radial dependence of the electronic current $\mathbf{j}(\mathbf{x})$, as calculated, for instance, in this work, as the external operator of maximum overlap, in order to obtain a main collective state. Comparison should then be made with real external excitations in order to evaluate the probability of exciting such a state.

CONCLUSIONS

Void excitations have been calculated in the framework of a fluid-dynamical model. The energies of the plasmons of various multipolarities were obtained, showing a good agreement with available experimental data.

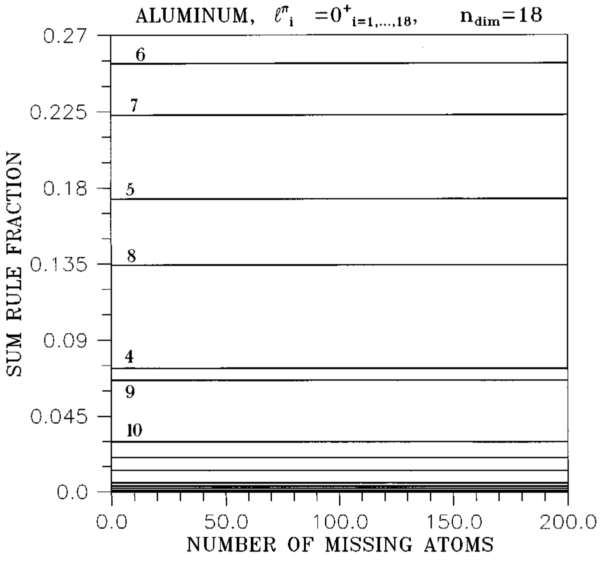

FIG. 8. Monopole sum rule exhaustion for the eigenmodes in aluminum, as a function of the number of the missing atoms in the cavity. We have ordered the states from the lowest to the highest energy.

Cavity excited states present interesting behavior concerning the onset of the collectivity: there is a minimum radius below which one cannot speak of a collective plasmon. It is seen that for hard metals, such as copper, collectivity remains distributed among many higher-lying modes, up to many hundreds of missing atoms, for the higher multipolarities. Such an effect, which is absent for clusters,[22] puts restrictions on the use of methods based on the hypothesis of a single collective state for small voids. The bulk limit for every multipolarity is correctly obtained, even with the sheer use of the sum rules satisfied by the model.

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*Permanent address: Instituto de Física, Universidade Federal do Rio de Janeiro, 21945 Ilha do Fundão, Rio de Janeiro, Brasil.

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