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ELECTRON-ION SCATTERING AND PLASMON DAMPING IN METALLIC CLUSTERS

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ЭЛЕКТРОН-ИОННОЕ РАССЕЯНИЕ И ПЛАЗМОННОЕ ЗАТУХАНИЕ В МЕТАЛЛИЧЕСКИХ КЛАСТЕРАХ

Processes of electron scattering on fine ionic structure leading to the decay of dipole plasmon oscillations in alkali metal clusters are investigated. The study is based on separation of the collective plasmon oscillations and single particle excitations. Coupling between these two types of electronic motions caused by electron-ion scattering leads to the plasmon damping. The relative contributions of elastic and inelastic electron-ion scattering to plasmon linewidth are considered. The results are compared with experimental data on cluster photoabsorption for sodium clusters of different size.

CLUSTER, PLASMON, SCATTERING, OSCILLATION, EXCITATION, DAMPING.

Исследована роль электрон-ионного рассеяния в затухании коллективных плазмонных возбуждений в кластерах щелочных металлов. Теоретическая модель основана на разделении коллективных плазмонных возбуждений электронов кластера, соответствующих осцилляциям центра масс электронов, и одночастичных электронных возбуждений в системе их центра масс. Перемешивание этих типов движения электронов вследствие электрон-ионного рассеяния ведет к затуханию плазмонных колебаний. Оценены сравнительные вклады упругого и неупругого электрон-ионного рассеяния в уширение плазмонного резонанса. Результаты сравниваются с экспериментальными данными по ширинам плазмонных резонансов в спектрах фотопоглощения кластеров натрия.

КЛАСТЕР, ПЛАЗМОН, РАССЕЯНИЕ, КОЛЕБАНИЕ, ВОЗБУЖДЕНИЕ, ЗАТУХАНИЕ.

I. Introduction

The optical response of alkali-metal clusters is dominated by the surface dipole plasmon resonance [1, 2]. This collective electronic excitation corresponds to a coherent oscillation of the electronic cloud against the positively charged ionic background, i. e. to the vibration of electronic center of mass (CM). The position and the width of giant plasmon resonance has been experimentally determined for various sodium clusters in numerous experimental works on cluster spectroscopy [3–8]. An adequate theoretical prediction for the resonance position has been given within the Linear Response theory using either the Time Dependent Local Density Approximation (TDLDA) [9–11] or the Random Phase Approximation with Exchange (RPAE) [12–14]. However, in spite of intensive study, the fundamental questions concerning the origin of plasmon decay width is still not well understood.

In the first attempts to evaluate the plasmon resonance width, the nonhomogeneous broad-

ening of electron energy levels due to the thermal fluctuation of the cluster background has been considered [15–24]. This mechanism of the line broadening is connected with adiabatic dependence of electron energy upon the position of the ions. Therefore, the corresponding linewidth is not connected with the life time of electron excitations. The obtained plasmon width decreases with the cluster radius growth. This fact is easy to understand since the role of such adiabatic electron-ion coupling diminishes with the increase of cluster size vanishing in the bulk limit. On the other hand, the experimentally observed resonance width does not monotonically decrease as a function of cluster size. On the contrary, it periodically varies due to the shell effects in the range of $0.2 - 0.3$ eV [8]. Therefore, this contribution to the resonance width can be essential only for the very small clusters with less than tens of atoms.

Another approach considers the decay of collective plasmon mode via excitations of the single-particle electronic transitions [25]. This mechanism is well known in the theory of collective fermionic excitations in nuclear and plasma physics as Landau damping. The main question for Landau damping mechanism is the origin of the coupling interaction that is responsible for the relaxation of plasmon mode excitation energy among numerous electronic degrees of freedom. Indeed, for example, in the case of the homogenous infinite positive cluster background there is not such coupling interaction at all, and electron cloud can oscillate with plasmon frequency against positive background without any perturbation of its intrinsic motion and therefore without any damping. Therefore, possible relaxation of the collective plasmon excitation can be expected from the deviation of ionic background potential in real cluster from a pure homogenous positive infinite jellium, namely from the fine ionic structure and the cluster boarder.

The boarder of the cluster background has been traditionally considered in the past as the main source of the coupling interaction [25]. Electron scattering on the spherical cluster border leads to well-known inverse radius dependence of Landau damping width [26–28], $\Gamma = Cv_F/R$, where R is the cluster radius, v_F is the Fermi velocity of cluster valence electrons and C is a constant about one unit. However, this result is valid only for the relatively large clusters with more than thousand atoms, and this has been proved by a direct numerical calculations [29]. This simple formula is based on the assumption that the spectrum of dipole electron excitations is continuous and therefore it cannot be applied to the small metallic clusters with less than hundred atoms [28]. Indeed, for such small clusters, which will be considered in the present paper, the use of this formula strongly overestimates experimentally observed plasmon width [8].

Therefore, one can associate the plasmon width with electron scattering on the fine ionic structure. In the resent paper we propose a simple transparent analytical model in order to clarify the physical nature of the plasmon damping caused by electron-ion scattering. Our model is developed with the use of a new description of the collective plasmon excitation based on the separation of the center of mass (CM) and the intrinsic motion of delocalized valence electrons [30]. The method relies on the smallness of the CM oscillation amplitude compared to the cluster radius.

Considering the electron-ionic collisions, one can distinguish elastic electron-ion scattering and inelastic scattering on the ionic vibrations, phonons when the plasmon decay is accompanied by simultaneous emission or absorption of phonons. The last case has been studied in our previous paper [31]. Electron-phonon coupling yields the temperature dependent plasmon width that for the 100 K clusters amounts approximately to one fourth of the total plasmon width.

The present paper is focused on the elastic electron-ion scattering. We use the pseudopotential to describe the electron scattering on an isolated sodium atom and the simple Fermi gas model to describe the intrinsic single-particle excitations. For simplicity we consider only the spherical sodium clusters.

II. Collective Plasmon Mode

To distinguish the dipole plasmon mode from all other electron excitations it is convenient to separate the intrinsic and the CM electron coordinates. We will start with the total electron Hamiltonian of the cluster which

includes the electron kinetic energy, the energy of interelectronic Coulomb interaction and interaction with ionic background:

$$\widehat{H} = \sum_a \frac{\widehat{p}_a^2}{2} + \frac{1}{2}\sum_{a\neq b}\frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} + \sum_a V_{ion}(\mathbf{r}_a), \quad (1)$$

where $V_{ion}(\mathbf{r})$ is the potential of ionic background, the summation is performed over all the cluster valence electrons.

Let us designate the CM vector by $\mathbf{R}$ and the intrinsic electron coordinates, i. e. the electron coordinates in CM reference frame, by $\mathbf{r}'_a$:

$$\mathbf{R} = \frac{1}{N}\sum_a \mathbf{r}_a, \quad \mathbf{r}'_a = \mathbf{r}_a - \mathbf{R}, \quad (2)$$

where N is the number of valence electrons.

Similarly, the momentum of the center of mass motion is equal to $\widehat{\mathbf{P}} = \sum_a \hat{\mathbf{p}}_a$ and electronic momenta in the CM reference frame are $\widehat{\mathbf{p}}'_a = \hat{\mathbf{p}}_a - \widehat{\mathbf{P}}/N$ respectively. We separate the intrinsic and CM coordinates in Eq. (1) assuming that the amplitude of CM displacement $\mathbf{R}$ is much smaller than the cluster radius R_0 (we will demonstrate below that this condition is usually fulfilled). Radius of the cluster background we determine by standard expression $R_0 = r_s N_{at}^{1/3}$ [9, 11] using the Wigner – Seitz radius r_s of the bulk material ($r_s = 4$ a.u. for sodium) and the number of atoms in a cluster. So we can expand the potential of the ionic background $V_{ion}(\mathbf{r}'_a + \mathbf{R})$ in Eq.(1) in power series with respect to $\mathbf{R}$, and the total electron Hamiltonian (1) can be written as:

$$\widehat{H} = \widehat{H}' + \frac{\widehat{P}^2}{2N} + U(\mathbf{r}'_a, \mathbf{R}), \quad (3)$$

where $U(\mathbf{r}'_a, \mathbf{R})$ is alteration of V_{ion} under the displacement of the CM:

$$U(\mathbf{r}'_a, \mathbf{R}) = \sum_a (V_{ion}(\mathbf{r}_a) - V_{ion}(\mathbf{r}'_a)) = \\ = \sum_{n=1,a} \frac{1}{n!}(\mathbf{R}\nabla)^n V_{ion}(\mathbf{r}'_a). \quad (4)$$

Operator $\widehat{H}'$ is the Hamiltonian of intrinsic motion. It has the form of the total Hamiltonian (1) with natural replacement of all electronic coordinates and momenta by corresponding values in CM system.

Let us start with zero approximation which implies that CM and intrinsic electron motions are completely independent. This approximation is based on the following simple fact. Within the standard jellium model [9, 11] which treats the ionic background as the positive charge density $\rho_i = 3/4\pi r_s^3$ homogeneously distributed throughout the entire cluster volume, for sufficiently large cluster the coordinates of CM and intrinsic motion separate. Indeed, neglecting the electrons outside the cluster volume, i. e. the spill out electrons, and using the condition $\sum_a \mathbf{r}'_a = 0$, one immediately finds that

$$U(\mathbf{r}'_a, \mathbf{R}) = (4\pi\rho_i/3)R^2/2$$

and does not depend upon the intrinsic electron coordinates. Therefore, the CM oscillates in a pure parabolic potential with Mie frequency $\omega_{Mie} = r_s^{-3/2}$. As a result, one can write the total electron wave function as a product of wave functions of CM and intrinsic motions:

$$\Psi(\mathbf{r}_a) = \Psi(\mathbf{R})\Phi(\mathbf{r}'_a), \quad (5)$$

which assumes that the CM motion does not perturb the intrinsic wave function $\Phi(\mathbf{r}'_a)$, , i. e. the CM oscillates adiabatically with respect to all other electronic degrees of freedom.

According to the standard adiabatic theory [32], the wave function (5) turns out to be the eigen wave function of the total electron Hamiltonian (3). Here the wave function of intrinsic motion $\Phi(\mathbf{r}'_a)$ is the eigen wave function of the intrinsic Hamiltonian $\widehat{H}'$ with corresponding eigen energy ε_ν. The CM wave function $\Psi(\mathbf{R})$ is the eigen wave function of the effective plasmon Hamiltonian obtained as average of the total electron Hamiltonian (3) over intrinsic motion:

$$\widehat{H}_P = \frac{\widehat{P}^2}{2N} + U_{eff}(\mathbf{R}), \quad (6)$$

where the role of effective potential for CM motion $U_{eff}(\mathbf{R})$ is played by the diagonal matrix element of $U(\mathbf{r}'_a, \mathbf{R})$:

$$U_{eff}(\mathbf{R}) = \left\langle \Phi_\nu(\mathbf{r}'_a) \middle| U(\mathbf{r}'_a, \mathbf{R}) \middle| \Phi_\nu(\mathbf{r}'_a) \right\rangle. \quad (7)$$

Let us use the expansion (4) for $U(\mathbf{r}'_a, \mathbf{R})$. All odd terms vanish after the averaging over intrinsic wave function $\Phi_\nu(\mathbf{r}'_a)$. The first nonvanishing term corresponds to the pure oscillator potential

$$U_{eff}(\mathbf{R}) = N\frac{\omega_p^2 R}{2}, \ \omega_p^2 = \frac{4\pi}{3N}\int \rho_e \rho_i dV, \quad (8)$$

where ρ_e and ρ_i are the electronic and ionic densities, respectively. Here we consider spherical clusters with isotropic density distributions ρ_e and ρ_i. For homogeneous jellium distribution of ionic background with sharp edge

$$\rho_i = \frac{3}{4\pi r_s^3}\theta(R_0 - r). \quad (9)$$

Eq. (8) gives us

$$\omega_p = \omega_{Mie}\sqrt{1 - \frac{\delta N}{N}}, \quad (10)$$

where δN is the number of spill out electrons.

Thus, within this approximation the electron energy spectrum is given as the sum of intrinsic energies ε_ν and the energies of harmonic oscillations of CM

$$E_{n,\nu} = \varepsilon_\nu + \omega_p\left(n + \frac{1}{2}\right), \quad (11)$$

where n is the quantum number of oscillator state $\Psi_n(\mathbf{R})$, i. e. the number of excited plasmons.

Within the dipole approximation, external electromagnetic laser field acts only on the CM wave function and does not excite the intrinsic motion, i. e. $\nu = 0$. A time dependent electric field simply induces a transition from the 1s ground state to the 1p state of CM motion, ω_p above the ground state. Consequently, the many-body wave function (5) for the single plasmon excitation $|i\rangle$ is the product of this collective harmonic oscillation function $\Psi_{1p}(\mathbf{R})$ and the ground state many-body wave function $\Phi_0(\mathbf{r}'_a)$ depending only on the intrinsic coordinates, thus

$$\langle \mathbf{R}, \mathbf{r}'_a | i\rangle = \Psi_{1p}(\mathbf{R})\Phi_0(\mathbf{r}'_a).$$

The average displacement of the electronic CM for 1p state is equal to $\sqrt{\langle R^2\rangle} = \sqrt{3/2\omega_p N}$. For Na_{92} cluster the ratio $\sqrt{\langle R^2\rangle}/R_0 = 0.02$ and it decreases for the lager clusters as $N^{-5/6}$. This fact confirms the applicability of the performed power expansion (4). Besides the dipole surface plasmon mode, there are a lot of non-optically active excitations $|f\rangle$ of the intrinsic electron motion. In our notations, the corresponding many-electron wave function is written as

$$\langle \mathbf{R}, \mathbf{r}'_a | f\rangle = \Psi_{1s}(R)\Phi_\nu(\mathbf{r}'_a)$$

with the collective wave function being the 1s state of the CM harmonic oscillator and with wave function of intrinsic excitation ν.

III. Plasmon Damping

Within the zero approximation, we neglect the coupling terms in the total electron Hamiltonian Eqs. (3), (4) which cause the transitions between plasmon $|i\rangle$ and intrinsic $|f\rangle$ excitations. Formally, this coupling originates from the non-diagonal matrix elements of $U(\mathbf{r}'_a, \mathbf{R})$. The first term of the expansion $U(\mathbf{r}'_a, \mathbf{R})$ (4) provides the leading contribution to the coupling. Therefore, below we will keep only this coupling term in the expansion (4):

$$W(\mathbf{r}'_a, \mathbf{R}) = \sum_a (\mathbf{R}\nabla)V_{ion}(\mathbf{r}'_a). \quad (12)$$

This term corresponds to the additional time-dependent electromagnetic field arising in the CM system due to the plasmon oscillations. Note that within the jellium model potential $W(\mathbf{r}'_a, \mathbf{R})$ actually coincides with the well-known separable approximation for electron-electron interaction between dipole plasmon excitation and single particle electronic excitations in cluster [25]. The total Hamiltonian of the cluster $\hat{H}$ (3) now can be written as

$$\hat{H} = \hat{H}'(\mathbf{r}'_a) + \hat{H}_P(\mathbf{R}) + W(\mathbf{r}'_a, \mathbf{R}), \quad (13)$$

where $W(\mathbf{r}'_a, \mathbf{R})$ couples plasmon $|i\rangle$ and intrinsic $|f\rangle$ excitations.

The relaxation of plasmon excitation originates from the electronic transitions from optically excited state $|i\rangle$ to all possible final states $|f\rangle$ caused by the coupling term $W(\mathbf{r}'_a, \mathbf{R})$ in Hamiltonian Eq. (13). The rate of such transitions, i. e. the corresponding plasmon width Γ, we will calculate using the first-order time-dependent perturbation theory:

$$\Gamma = 2\pi\sum_f \left|\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i\rangle\right|^2 \delta(\varepsilon_f - \varepsilon_i). \quad (14)$$

The transition matrix element $\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i\rangle$ in Eq.(14) is given by the product of an oscillator matrix element $\langle 1p | \mathbf{R} | 1s\rangle = 1/\sqrt{2N\omega_p}$ [32] and a matrix element of intrinsic motion:

$$\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i\rangle = \frac{\left\langle \Phi_\nu(\mathbf{r}'_a)\left|\frac{d}{dz'}V_{ion}(\mathbf{r}'_a)\right|\Phi_0(\mathbf{r}'_a)\right\rangle}{\sqrt{2N\omega_p}}. \quad (15)$$

Here the axe z is chosen along the direction of plasmon oscillations.

For homogenous infinite positive jellium background, $V_{ion}(\mathbf{r}') = \omega_p^2 r'^2 / 2$, matrix element (15) apparently vanishes. Indeed, in this case $\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i \rangle$ is proportional to the dipole matrix element of the intrinsic motion which equals to zero by the definition of the CM frame. In the real cluster, background potential V_{ion} differs from the pure harmonic pattern due to the fine ionic structure and the cluster border.

To estimate the matrix element $\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i \rangle$ let us assume that the excitation in the intrinsic electronic system is a pure particle-hole transition and that particles and holes inside the cluster are plane waves in the Fermi gas model. We represent the ionic potential V_{ion} as a sum of pseudopotentials v_p of each ion

$$V_{ion}(\mathbf{r}) = \sum_a v_p(\mathbf{r} - \mathbf{R}_a). \qquad (16)$$

Here $\mathbf{R}_a$ denotes the position of the a-th ion.

However, the simple homogeneous Fermi gas model should be improved in order to reproduce the main features of intrinsic excitation in real cluster. Indeed, when we represent the intrinsic excitation in the cluster by a particle-hole transition of the Fermi gas using the plane waves for electronic wave functions, we do not take into account the electron confinement as well as many-body effects. In order to introduce the electron confinement, we will restrict the integration in the matrix element (15) by the cluster sphere. Electron correlation leads to the screening pseudo-potentials by cluster delocalized electrons. We will take into account this many-body effect by using the permittivity of homogeneous Fermi gas. Also the employed model should be corrected in order to correspond to intrinsic excitations. Namely, the dipole matrix element for particle-hole transitions should be zero in the CM frame. Otherwise matrix element $\langle f | W | i \rangle$ is not zero even for the pure harmonic background potential $V_{ion}(\mathbf{r}') = \omega_{Mie}^2 r'^2 / 2$. We will correct this effect by the subtraction the linear term

$$d(\omega_{Mie}^2 r'^2 / 2) / dz' = \omega_{Mie}^2 z'$$

from the operator in the matrix element (15). Within these assumptions, matrix element (15) is written as

$$\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i \rangle = \\ = \frac{1}{\sqrt{2N\omega_p}\,\varepsilon(q)} \int_{r<R_0} e^{iq\mathbf{r}} \left(\frac{dV_{ion}(\mathbf{r})}{dz} - \omega_{Mie}^2 z \right) d\mathbf{r}^3, \qquad (17)$$

where $q = p_e - p_h$ is the moment of electron-hole pair, $\varepsilon(q)$ is the permittivity of homogeneous Fermi gas:

$$\varepsilon(q) = 1 + \frac{4p_F}{\pi q^2}. \qquad (18)$$

It will be convenient to extend the integration in the right hand side of Eq.(17) over the infinite volume. It can be done by the addition and subtraction of the integral of

$$\exp(iq\mathbf{r}) dV_{ion}(\mathbf{r})/dz$$

outside the cluster border, $r > R_0$. For simplicity, outside the cluster where the fine ionic structure is not so important, we will replace the real background potential $V_{ion}(\mathbf{r})$ by the spherical jellium model potential:

$$V_{jell}(\mathbf{r}) = \begin{cases} \frac{\omega_{Mie}^2}{2}(r^2 - 3R_0^2), & r < R_0; \\ -\frac{N}{r}, & r > R_0. \end{cases} \qquad (19)$$

Then the matrix element (17) becomes equal to

$$\langle f | W(\mathbf{r}'_a, \mathbf{R}) | i \rangle = \\ = \frac{q_z}{\sqrt{2N\omega_p}\,\varepsilon(q)} (V_{ion}(\mathbf{q}) - V_{jell}(\mathbf{q})), \qquad (20)$$

where

$$V_{jell}(\mathbf{q}) = \frac{12\pi N}{q^3 R_0} j_1(qR_0) \qquad (21)$$

is the Fourier transform of the jellium potential (j_1 is the spherical Bessel function);

$$V_{ion}(\mathbf{q}) = v_p(\mathbf{q}) F(\mathbf{q}) \qquad (22)$$

is the Fourier transform of the ionic background potential, $v_p(\mathbf{q})$ is the Fourier transform of the pseudo-potential,

$$F(\mathbf{q}) = \sum_{a=1}^{N} e^{i\mathbf{q}\mathbf{R}_a} \qquad (23)$$

is the structure formfactor of the ionic background.

Using Eq.(20) one obtains from Eq.(14):

$$\Gamma = \frac{2\pi}{N\omega_p}\int \frac{d^3p_e d^3p_h}{(2\pi)^6}(p_{e_z} - p_{h_z})^2 \times \\ \times \left|V_{ion}(\mathbf{p}_e - \mathbf{p}_h) - V_{jell}(\mathbf{p}_e - \mathbf{p}_h)\right|^2 \times \\ \times\delta\left(\frac{p_e^2}{2} - \frac{p_h^2}{2} - \omega_p\right). \quad (24)$$

Here we integrate over hole momentum below the Fermi level $p_h < p_F = 1.92/r_s$ and over the electronic momentum above the Fermi sphere $p_e > p_F$.

Note that Eq.(24) does not account for the Landau damping connected with electron scattering on the cluster surface. Indeed, in the case of homogenous jellium background, $V_{ion}(\mathbf{q}) = V_{jell}(\mathbf{q})$, Eq.(24) gives zero width identically. The non-zero result requests more detailed description of electronic wave function near the cluster surface. According to Eq. (15), the coupling matrix element arises in the case of $V_{ion}(\mathbf{q}) = V_{jell}(\mathbf{q})$ from the region of spill-out electrons where in our simple model electron wave function is put equal to zero.

We perform numerical calculations of plasmon linewidth according to Eq.(24) for series of sodium clusters Na_N of different size $8 \le N \le 93$ with forms close to spherical. The results are presented in Fig. 1 by triangles (see curve *2*).

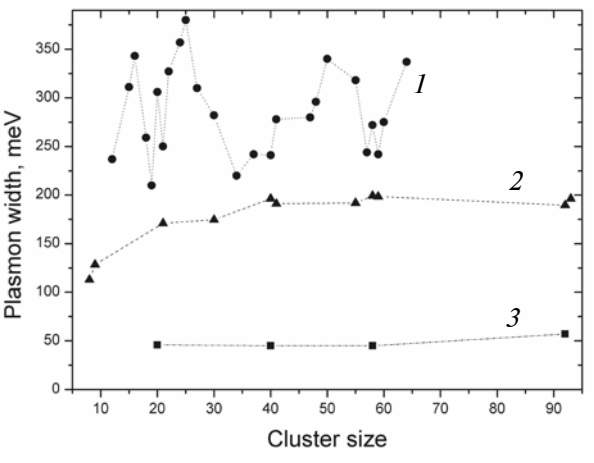

Fig. 1. Plasmon resonance widths in sodium clusters as a function of cluster size: *1* – experimental data on photoabsorption spectra (FWHM); *2*, *3* – the calculated contributions of elastic (*2*) and inelastic (*3*) electron-ion scattering to plasmon width

The following pseudo-potential $v_p(r)$ for sodium has been used:

$$v_p(r) = -\frac{1}{r} + B\frac{\exp(-\beta r^2)}{r} + C\exp(-\gamma r^2), \quad (25)$$

where $B = 1.0$, $C = 0.5$, $\beta = 0.35$, $\gamma = 0.8$, the numbers are given in atomic units.

Our calculations demonstrate that this contribution to plasmon width increases with cluster size for small clusters ($N \le 40$). For larger cluster, the increase saturates as linewidth approaches the bulk value limit. In the limit of bulk sodium, the electron interaction with regular ionic crystal structure results in the band energy spectrum. Plasmon damping associates in this case with interband photoexcitation at plasmon resonance energy ω_p and amounts to 173 meV [8]. This value is in a good agreement with results of our calculations for large clusters.

Note that in the model of electron-ion coupling developed here, the ionic structure considered as frozen. It means that only the elastic electron-ion scattering is taken into account. Indeed, according to Eqs. (14), (24) the energy of collective excitation ω_p is transfered entirely to the single particle excitations. Besides the elastic electron-ion scattering, one can also consider the inelastic scattering on the ionic vibrations, phonons, when the plasmon decay is accompanied by simultaneous emission or absorption of phonons. The plasmon width associated with electron-phonon interaction have been studied in our paper [31]. This contribution to the plasmon width is temperature dependent. For comparison with experimental data on plasmon linewidth [8], we calculated electron-phonon contribution at the same cluster temperature $T = 100$ K as at the photoabsorption measurements. Electron interactions with volume and surface phonon modes both give size dependent contributions to plasmon width. However, their sum shown in Fig. 1 by squares (see curve *3*) does not almost depend on cluster size. Our calculations demonstrate that inelastic electron-ion scattering provides a few times smaller contribution to the plasmon width than

the elastic scattering does.

The experimentally observed plasmon width obtained from the analysis of Na_N photoabsorption spectra [8] are shown in Fig. 1 by circles (see curve *1*). The size dependence of experimental width is non-monotone. For comparison with our theoretical calculations, we should concentrate on spherical clusters with $N = 8, 20, 40, 58, 92$. These clusters have the lowest plasmon width. The joint contribution of elastic and inelastic electron-ion scattering to plasmon width correlates with experimental linewidth for spherical clusters. For non-spherical clusters, experimental linewidth exceeds the calculated values by 100–150 meV. This discrepancy should be attributed to the electron scattering on cluster surface which is not taken into account in our calculations. The good agreement between our calculations and experimental data achieved for closed shell clusters testify that this contribution is not essential for spherical clusters. The well-known formula $\Gamma = C v_F / R_0$ [25] for plasmon width associated with electron scattering on cluster boarder strongly overestimates the effect because it does not take into account that only spill-out electrons contribute to this type of plasmon damping. For non-spherical clusters the effect of electron scattering on cluster surface is much larger due to the mixture of electronic states with different angular momenta. In this case, the dipole collective plasmon excitation decays into numerous single particle excitations with various angular momenta. It leads to much more effective plasmon damping than in the case of spherical clusters where the number of single particle excitations involved in plasmon damping is restricted by the dipole ones.

IV. Conclusion

The plasmon damping associated with electron scattering on the fine ionic structure is described within a simple analytical model. The developed model is based on the separation of the collective plasmon and single particle electron excitations. The coupling between these excitations caused by electron scattering on fine ionic structure leads to plasmon damping. We demonstrate that elastic electron-ion scattering is much more essential than the inelastic electron scattering on ionic vibrations. In the case of spherical clusters it provides the leading contribution to the total plasmon width. In the case of non-spherical clusters the electron scattering on cluster surface is also essential.

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