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RESPONSE OF ELECTRONIC SURFACE IN METAL CLUSTERS WITHIN A PHASE SPACE APPROACH

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The surface vibrations of the valence electrons in spherical alkali-metal clusters are studied within a phase space approach which is based on the Landau-Vlasov kinetic equation. The linear response theory is used. The proposed method allows for the analysis of the contribution of the electron orbits with different angular momentum into the strength function. The strength function for the electronic surface vibrations is investigated. Applications to the dipole collective excitations in sodium clusters are presented. We reproduce both the surface and volume branches of the dipole resonance. The analysis is carried out for the electron-electron collision integral taking into account the retardation effects. Enhancement of the two-electrons scattering rate in two orders of magnitude due to the memory effects is shown.

In recent years collective resonances and response properties of electrons in metal clusters are the subjects of wide investigations ([1-4] and references therein). Many experimental results have been explained within the framework of the jellium model. This model belongs to the class of mean- fields models. In the jellium model the valence electrons are assumed to move in a self- consistent field formed by the ions of cluster. The microscopic framework for description of the collective resonances with high frequencies within mean- field theory are the theories like random- phase approximation (RPA) [5-7]. However the calculations based on such microscopic approaches, in particular for large clusters, are greatly time- consuming. There are semiclassical models of description of multipole vibration in clusters. The semiclassical extension of the RPA sum- rule approach was successfully used in [3,4,8] for estimations of the position and width of the collective resonances. A semiclassical theory of linear response based on the Vlasov- Landau kinetic equation for a Fermi- gas with an effective coordinate dependent residual interaction was applied in [9-10] to the study of surface oscillations and photoabsorption in small metal spheres.

Semiclassical methods seem to be the most suitable for the investigation of properties of the multiparticle systems. They allow to obtain analytical results and due to this to study average properties of the systems in a transparent way. It should be mentioned that as in RPA, a mean- field formed by all particles is also incorporated in the Vlasov- Landau transport equation. Moreover, this kinetic approach is very suitable for description of damping of collective modes. A semiclassical dynamics like Landau-Vlasov includes the Landau damping (the fragmentation) as well as the particle scatterings. Thus in this approach electron- electron and electron- ion collisions can be taken into account to include their associated collision integrals to the kinetic equation.

The dynamical phenomena in finite Fermi systems related with different branches of physics have an instructive similarities. It was pointed out in ref. [1,3], that there is an analogy between the two physical types of dipole collective resonances in small metal clusters and the nature of nuclear giant isovector dipole resonance. The study of this nuclear resonance carried out within

a hydrodynamical description in ref. [11] led to conclusion that it is a suitable combination of two collective modes: a compressional one proposed by Migdal [12] and by von Steinwedel and Jensen (MSJ) [13], and a purely translational one proposed by Goldhaber and Teller (GT) [14]. The GT mode is similar to the surface oscillations of the valence electrons in a metal cluster, whereas the MSJ mode is analogous of the volume plasmon.

For studying the collective modes related with excitations in the surface region of a system it is convenient to use explicitly macroscopic collective variables describing the displacement of the effective surface of a system from its equilibrium position. Such description (the Fermi liquid drop model for a small vibrations) has been formulated within the phase space approach in ref.[15] and recently it was employed to study the multipole vibrations of nuclear surface [16]. In the present paper we consider the strength distribution of electronic surface vibrations in metal clusters around a spherical equilibrium shape by extending the phase space approach proposed in [15,16].

In Sect.1 we find the surface response function of valence electrons system in alkali cluster to a periodic external force. In Sect.2 we extend our model to include collisional effects. We obtain expression for the relaxation time due to electron- electron scattering as function of frequency of the collective mode and temperature. In Sect.3 we look at the properties of imaginary part of dipole response function (the dipole strength function) for the sodium clusters. To understand the nature of the collective modes we give an analysis of the partial contribution of electron orbits with different angular momentum into the strength function. Finally, our study is concluded in Sect.4.

1. Surface response of cluster valence electrons

We will assume that the electrons in a metal cluster behave like a Fermi liquid (an interacting Fermi gas) bound by the surface

$$r = R + \delta R(\vartheta, \varphi, t), \quad (1)$$

which is the sphere with radius R in equilibrium. The radius R is related with the number N of valence electrons in the cluster by $R = r_s N^{1/3}$, where r_s is the Wigner-Seitz parameter, which characterizes the metal. The macroscopic variable $\delta R(\vartheta, \varphi, t)$ describes the local displacement of the electronic surface $R(\vartheta, \varphi, t)$ from its equilibrium position.

A change in R induces motion of the electrons inside the sphere. The latter can be represented by a variation of the distribution function $\delta n(\vec{r}, \vec{p}, t)$ in the phase space. The equation of motion for $\delta n(\vec{r}, \vec{p}, t)$ is given by a linearized Vlasov- Landau equation [17]

$$\frac{\partial}{\partial t} \delta n(\vec{r}, \vec{p}, t) + \vec{v} \frac{\partial}{\partial \vec{r}} \left[\delta n(\vec{r}, \vec{p}, t) - \frac{dn_0}{d\epsilon} \int d\vec{r}' \vec{p}' \mathcal{F}(\vec{r}, \vec{p}; \vec{r}', \vec{p}') \delta n(\vec{r}', \vec{p}', t) \right] = J[\delta n(\vec{r}, \vec{p}, t)]. \quad (2)$$

Here $\vec{v} = \vec{p}/m$ and $J[\delta n(\vec{r}, \vec{p}, t)]$ is the linearized collision integral, see Sect.3. The amplitude $\mathcal{F}(\vec{r}, \vec{p}; \vec{r}', \vec{p}')$ describes the interactions of the electrons in the cluster. Below to study the surface response of electronic system we neglect in eq. (2) the deviation the self-consistent potential in the bulk of the system by putting $\mathcal{F}(\vec{r}, \vec{p}; \vec{r}', \vec{p}') = 0$. The possibility of the description of collective excitations will be achieved by suitable choice of the boundary conditions. Following [15] the equation (2), valid inside a system at $r < R$, is accomplished by "mirror reflection" boundary conditions at the moving surface (1)

$$[\delta n(\vec{r}, \vec{p}_\perp, p_r, t) - \delta n(\vec{r}, \vec{p}_\perp, -p_r, t)] \Big|_{r=R} = -2p_r \frac{dn_0}{d\epsilon} \frac{\partial}{\partial t} \delta R(\vartheta, \varphi, t), \quad (3)$$

where p_r is the radial momentum and $\vec{p}_\perp = (0, p_\vartheta, p_\varphi)$.

An essential property of a finite Fermi system having a free surface is that the motion of the surface should be consistent with the motion of the particles inside the system. This can be achieved by means of the following "subsidiary condition":

$$P_{rr}(\vec{r}, t) \Big|_{r=R+\delta R(\vartheta, \varphi, t)} = P_S(\vartheta, \varphi, t) + F_L(\vartheta, \varphi, t). \quad (4)$$

Here $P_{rr}(\vec{r}, t)$ is the normal component of the momentum flux tensor $P_{ik}(\vec{r}, t)$, see e.g. [17], Ch.1,

$$P_{ik}(\vec{r}, t) = \int \frac{d\vec{p}}{h^3} p_i v_k \delta n(\vec{r}, \vec{p}, t),$$

This component describes the forces acting on the electronic moving surface inside of the system, in particular, it is connected with compression of the electron density. The additional pressure $P_S(\vartheta, \varphi, t)$ caused by the resistance against the displacement of the effective surface of the electrons distribution from the equilibrium one. We assume that $P_S(\vartheta, \varphi, t)$ is related with the corresponding part of the electronic surface energy in the same way as in droplet model [11]. It can be written as

$$P_S(\vartheta, \varphi, t) = \frac{Q}{2\pi r_s^2 R^2} \delta R(\vartheta, \varphi, t).$$

Here Q is the stiffness coefficient against the electronic surface displacement. To estimate this coefficient we will assume that it is proportional to the symmetry energy one J ($Q = \alpha J$) as it was found in the nuclear case [11] (where $\alpha \approx 0.5$). Then by means of the formula for total energy of a charged metallic cluster with N atoms and Z valence electrons [4] we can find from the energy term proportional to $(Z - N)^2$ the symmetry energy coefficient in metal clusters as

$$J = \frac{e^2}{r_s N^{2/3}} = \frac{14.3987}{r_s N^{2/3}} \text{ eV}, \quad (5)$$

where e is the electron charge.

In eq.(4) we have also involved an external pressure $F_L(\vartheta, \varphi, t)$. This has been done simply to enable us identify later the response of the system to such an external source and thus to benefit from the tools of linear response theory. For the present study, the $F_L(\vartheta, \varphi, t)$ is chosen in the following form

$$F_L(\vartheta, \varphi, t) = \sum_M F_{LM}(\omega) Y_{LM}(\vartheta, \varphi) \cos(\omega t) \exp(\eta t) \quad (6)$$

with $\eta = +0$ representing an infinitesimally small quantity to guaranty that the external field is turned on adiabatically at $t = -\infty$.

To find solutions of (2)-(3) it is convenient to change variables (\vec{r}, \vec{p}) to a new set of variables $(r, \epsilon, l, \alpha, \beta, \gamma)$ as proposed in [18],

$$(\vec{r}, \vec{p}) \rightarrow (r, \epsilon, l, \alpha, \beta, \gamma) \quad (7)$$

The new variables are particle energy $\epsilon = \epsilon_0$, particle angular momentum $l = |\vec{r} \times \vec{p}|$, radius r and Euler angles (α, β, γ) . The Euler angles are defined by the rotation of the laboratory frame (x, y, z) to (x', y', z') with \hat{z}' along \vec{l} and \hat{y}' along \vec{r} . Now the distributions of particles with positive radial velocities $\delta n^+(r, \epsilon, l, \alpha, \beta, \gamma, t)$ and with negative ones $\delta n^-(r, \epsilon, l, \alpha, \beta, \gamma, t)$ are considered separately.

Of interest are those solutions of eqs. (2)-(3) which are consistent to the special form of the external pressure (6). Thus we may write :

$$\delta R_L(\vartheta, \varphi, t) = \operatorname{Re} \left[\sum_M \delta R_{LM}(\omega) Y_{LM}(\vartheta, \varphi) \exp(-i\omega t) \right] \quad (8)$$

In terms of the new variables (7) these solutions can be written as

$$\delta R_L(\vartheta, \varphi, t) = \operatorname{Re} \left[\sum_{M,N} \delta R_{LM}(\omega) Y_{LN} \left(\frac{\pi}{2}, \frac{\pi}{2} \right) (\mathcal{D}_{MN}^L(\alpha, \beta, \gamma))^* \exp(-i\omega t) \right] \quad (9)$$

where we used the following expansion:

$$Y_{LM}(\vartheta, \varphi) = \sum_{N=-L}^L (\mathcal{D}_{MN}^L(\alpha, \beta, \gamma))^* Y_{LN} \left(\frac{\pi}{2}, \frac{\pi}{2} \right) \quad (10)$$

For the $\delta n(\vec{r}, \vec{p}, t)$ we seek for \mathcal{D} -functions expansion of the form:

$$\begin{aligned} \delta n_L(\vec{r}, \vec{p}, t) &= \frac{dn_0}{d\epsilon} \operatorname{Re} \left[\sum_{M,N} [f_{N,LM}^+(r, \epsilon, l, \omega) + f_{N,LM}^-(r, \epsilon, l, \omega)] \times \right. \\ &\quad \left. \times (\mathcal{D}_{MN}^L(\alpha, \beta, \gamma))^* \exp(-i\omega t) \right]. \end{aligned} \quad (11)$$

Functions $f^\pm(r, \epsilon, l, \omega)$ represent a change of the local energy for particles with angular momentum l at the distance r from the centre of the system. They describe the Fermi surface distortions.

Using in eq. (2) the new variables (7) and taking into account the expansion (11) for $\delta n_L(\vec{r}, \vec{p}, t)$ we obtain a system of the differential equations over r for the functions f^\pm . Their solution is found to be:

$$\begin{aligned} f_{N,LM}^\pm(r, \epsilon, l, \omega) &= \frac{\exp[\pm i(\omega \tau(r, \epsilon, l) - N \gamma(r, \epsilon, l))]}{\sin[(1/2)(\omega T(R, \epsilon, l) - N \Gamma(R, \epsilon, l))]} Y_{LN} \left(\frac{\pi}{2}, \frac{\pi}{2} \right) \times \\ &\quad \times \omega p(R, \epsilon, l) \delta R_{LM}(\omega). \end{aligned} \quad (12)$$

Here $p(r, \epsilon, l) = mv(r, \epsilon, l)$, where

$$v(r, \epsilon, l) = [(2/m)(\epsilon - l^2/(2mr^2))]^{1/2} \quad (13)$$

$$\tau(r, \epsilon, l) = \int_{r_1}^r dr' \frac{1}{v(r', \epsilon, l)} \quad (14)$$

$$\gamma(r, \epsilon, l) = \int_{r_1}^r dr' \frac{l}{mr'^2} \frac{1}{v(r', \epsilon, l)} \quad (15)$$

$$T(R, \epsilon, l) = 2\tau(R, \epsilon, l) \quad (16)$$

and

$$\Gamma(R, \epsilon, l) = 2\gamma(R, \epsilon, l). \quad (17)$$

We may now present the solutions (9) in terms of response function $\chi_L(\omega)$. The latter may be defined as :

$$\delta R_{LM}(\omega)/R = -\chi_L(\omega) F_{LM}(\omega). \quad (18)$$

With the help of (4) the response function $\chi_L(\omega)$ is found to be:

$$\chi_L(\omega) = \left[-\chi_{int}^L(\omega) - \frac{Q}{2\pi r_s^2 P_0 R} \right]^{-1}. \quad (19)$$

Here $\chi_{int}^L(\omega)$ is the so-called internal response function [17] given by

$$\chi_{int}^L(\omega) = -\frac{60\pi}{2L+1} \frac{\omega R}{v_F} \sum_{N=-L}^L |Y_{LN}(\frac{\pi}{2}, \frac{\pi}{2})|^2 \times \int_0^1 d\lambda \lambda (1-\lambda^2) ctg \left[\frac{\omega R}{v_F} (1-\lambda^2)^{1/2} - N \arccos \lambda \right]. \quad (20)$$

In eq.(20) the equilibrium pressure of the Fermi gas $P_0 = (2/5)\epsilon_F \rho_0$ and the dimensionless electron angular momentum $\lambda = l/(p_F R)$ are introduced. In (19) the additional pressure $P_S(\vartheta, \varphi, t)$, see (4), is used in the form (5).

The poles of the function (19) determine the eigenfrequencies of the collective oscillations in electronic system. In the section 4 we will study the properties of the imaginary part of the response function (19) for the dipole vibrations of the alkali clusters.

2. The inclusion of collisions

For small deviations from a Fermi sphere the two- electron collision integral J_c in (2) is the linearized collision integral of the form [19]

$$St(\vec{p}, \vec{r}, T) = \int \frac{d\vec{p}_2 d\vec{p}_3 d\vec{p}_4}{(2\pi\hbar)^6} \int d\vec{r}' \int_{-\infty}^T dt \exp \left\{ \frac{\alpha(t-T)}{\hbar} \right\} \quad (21)$$

$$w(\{\vec{p}_k\}, \{n_j(\vec{r}', t)\}) Q(\{n_j(\vec{r}', t)\}) P(t, T; \vec{R}', \vec{r}, \{\vec{p}_j\}). \quad \alpha \rightarrow +0,$$

which takes into account the retardation (memory) effects, i.e. this collision integral at the instant of time T is formed by particle interactions at all preceding instant of time t . Departure of particles from one-particle states at the instant t is determined by the probability $w(\{\vec{p}_k\}, \{n_j(\vec{r}', t)\})$ of electron collisions and the balance of populations $Q(\{n_j(t)\})$ of one-particle states:

$$Q(\{n_j\}) = \bar{n}_1 \bar{n}_2 n_3 n_4 - n_1 n_2 \bar{n}_3 \bar{n}_4, \quad \bar{n} \equiv (1 - n), \quad (22)$$

where $n_j \equiv n(\vec{p}_j, \vec{r}')$, $n_1 \equiv n(\vec{p}, \vec{r}')$. The quantity

$$P(t, T; \vec{r}', \vec{r}, \{\vec{p}_j\}) = \frac{1}{(2\pi\hbar)^4} \cos \left\{ \frac{1}{\hbar} \left[\int_t^T dt' \Delta\epsilon(\vec{r}', t') - \Delta\vec{p}(\vec{r}' - \vec{r}') \right] \right\}, \quad (23)$$

determines the relative contribution of particles that do not undergo additional collisions during the time interval from t to T ; $\Delta\vec{p} = \vec{p}_1 + \vec{p}_2 - \vec{p}_3 - \vec{p}_4$, $\Delta\epsilon = \epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4$, where $\epsilon_j \equiv \epsilon(\vec{p}_j, \vec{r}, t)$ is the self-consistent single-particle energy. The factor $\exp[-\alpha(T-t)/\hbar]$ in Eq. (21) explicitly takes into account the principle of weakening of initial correlations. The probability $w(\{\vec{p}_k\}, \{n_j(\vec{r}', t)\})$ of particle scattering at the point \vec{r}' can depend on the distribution function due to dynamical polarisability of the electron medium [20-22]. It means that the probability w

will be the frequency- dependent $w \equiv w_\omega$, when nonequilibrium component of the distribution function varies in time according to the harmonic law $\delta f \sim \exp[-i\omega t]$.

In the general case, the total dynamic part of this collision integral consists of three terms

$$J_c = \delta St_n + \delta St_\epsilon + \delta St_w. \quad (24)$$

The first term δSt_n is connected with the variation of the distribution function δn . The second one δSt_ϵ is governed by a variation of the mean field. The third term δSt_w results from the screening effect for the free two-body scattering in hot Fermi system due to high frequency collective vibrations. In the range of low frequency $k_B T \gg \hbar\omega$, where k_B is the Boltzmann constant, the term δSt_w is zero. At present the term δSt_w is rather poorly studied in kinetic theory.

As discussed in Refs. [23-25], instead of Eq. (21) we can use as a good approximation simplified collision integral within the relaxation time approximation of the following form

$$J_c(\delta n) = \frac{\delta n(\vec{r}, \vec{p}, t) - \hat{B}\delta n(\vec{r}, \vec{p}, t)}{\tau_c}, \quad (25)$$

for the calculation of the damping properties of collective vibrations in Fermi-liquid. Here operator \hat{B} provides for satisfying of the momentum and energy conservation laws [26-28]: $\hat{B}\delta n \equiv (\delta n)|_0 + (\delta n)|_1$, where $(\delta n)|_l$ is the dynamical component of a distribution function in the case of the deformation of the Fermi surface with the multipolarity l . Ignoring term $\hat{B}\delta n$, we have an expression for the collision integral commonly used in the relaxation time approximation

$$J_c(\delta n) = \frac{\delta n(\vec{r}, \vec{p}, t)}{\tau_c}, \quad (26)$$

The collective relaxation time τ_c is frequency and temperature dependent $\tau_c \equiv \tau_c(\omega, T)$. The frequency dependence of τ_c is due to the retardation effects in the collision integral. The dependence on temperature results from a smeared out behavior of the equilibrium distribution function near the Fermi momentum [23-25].

Strictly speaking, a physical interpretation of the quantity τ_c in Eqs. (25), (26) depends on the value $(\omega\tau_c)$ [23,24]. Specifically, in the regime of rare collisions ($\omega\tau_c \gg 1$) the time ($\tau_c \equiv \tau_c^{(r)}$) is a collective relaxation time in the case of the deformation of the Fermi surface with very large multipolarity. In the regime of frequent collisions ($\omega\tau_c \ll 1$) the quantity ($\tau_c \equiv \tau_c^{(f)}$) is the relaxation time in the case of a quadrupole deformation of the Fermi surface.

The magnitudes of $\tau_c^{(r)}$ and $\tau_c^{(f)}$ differ by the factor of d_2 ($\tau_c^{(r)} = d_2\tau_c^{(f)}$) which is equal to [25]

$$d_2 = \langle w\Phi_2 \rangle / \langle w \rangle, \quad (27)$$

where w is the probability of scattering of nucleons near the Fermi surface; the function Φ_2 defines the angular constraints for nucleon's scattering within the distorted layers of the Fermi surface with quadrupole multipolarity and brackets denote the averaging over angles which determined by the momentum of the colliding particles. If the probability w of the two-particles scattering is isotropic than a magnitude of d_2 is equal to $4/5=0.8$. In fact, this value d_2 defines the accuracy of using Eq. (25) as the two-body collision integral irrespective of the rate of two-body collisions.

The quantity $\tau_c^{(f)}$ is the relaxation time for the total number of collisions

$$N(\hat{p}) \equiv \int_0^\infty \delta St(\hat{p}, \epsilon_p) d\epsilon_p \quad (28)$$

in the direction $\hat{p} = \vec{p}/p$ in a unit time. The time $\tau_c^{(f)}$ is also the relaxation time for viscosity in the regime of fast collisions [23-29]. Due to the Landau's prescription [32] (see also [25-27] and the references therein) for calculation the coefficient of absorption of high-frequency vibrations (zero sound) in a Fermi liquid, the temperature and frequency dependence of $\tau_c^{(f)}$ will be proportional to the function

$$\Psi(\omega, T) \equiv - \int_0^{+\infty} d\epsilon_{0,1} \int_0^{+\infty} d\epsilon_{0,2} \int_0^{+\infty} d\epsilon_{0,3} \int_0^{+\infty} d\epsilon_{0,4} \quad (29)$$

$$Q(\{n_{0,j}\}) \delta(\epsilon_{0,1} + \epsilon_{0,2} - \epsilon_{0,3} - \epsilon_{4,0} + \hbar\omega) 6 / (\hbar\omega(k_B T)^2).$$

Using the standard method of calculating integrals over the momenta in Fermi liquids we obtain from (21)-(24), (28) the following expression for the relaxation time for collective motion at low frequency $k_B T \gg \hbar\omega$ (the thermal relaxation time) in the case of a quadrupole deformation of the Fermi surface [25]

$$\tilde{\tau}_2(T)/\hbar = \alpha(k_B T)^{-2}, \quad [k_B T, \alpha \text{ in eV}], \quad (30)$$

where the quantity α

$$\alpha = 12\pi^2 / (\hbar(m^*/\hbar^2)^3 \langle w \rangle) = 5\mu^2 / (4\pi^2 \rho v_F \sigma). \quad (31)$$

This expression is valid at low temperatures $k_B T \ll \mu$, where μ is the chemical potential, $\mu \approx \epsilon_F$ for $k_B T \ll \epsilon_F$. In Eq. (31) m^* is the effective electron mass, σ is the spin averaged electron - electron cross section, ρ is the density of electrons, v_F is the velocity of Fermi. We used also the value 4/5 for d_2 (see (27)). The relaxation time for collective motion at arbitrary frequency ($\tau_c^{(r)}(\omega, T)$) is obtained after division of the thermal time (30) by the function Ψ (29). As a result we have

$$\frac{1}{\tau_c(\omega, T)} \approx \frac{1}{\tau_c^{(r)}(\omega, T)} \equiv \frac{1}{\tau_2(\omega, T)d_2} = \frac{5}{4\tilde{\tau}_2(T)} \Psi(\omega, T), \quad (32)$$

In the case of low temperatures and frequencies in comparison with the chemical potential ($k_B T, \hbar\omega \ll \mu$) the function Ψ (29) is equal to

$$\Psi(\omega, T) = 1 + (\hbar\omega / (2\pi k_B T))^2. \quad (33)$$

The equations (32), (33) lead to Landau's result [30] for the coefficient of absorption of zero sound in the high-frequency limit.

Note that the situation $\hbar\omega \ll \mu$ can be achieved at collective motion in liquid helium [27] and nuclear matter [25]. In the discussed case of plasmon vibration in metallic clusters the energies of collective vibrations and the Fermi energy have almost the same values $\hbar\omega \approx \mu \approx \epsilon_F$ [3,20]. In this situation the expression (33) should be modified. Using the result for the energy integral in (29) from [31], we have, when $\hbar\omega \approx \mu \approx \epsilon_F$

$$\Psi(\omega, T) \approx (1 + (\hbar\omega / (2\pi k_B T))^2) / (1 + \frac{1}{6}(\hbar\omega/\mu)^2 / (1 + 2(k_B T/\mu)^2)). \quad (34)$$

The relaxation time for collective motion at arbitrary frequency can be obtained by combining Eqs. (30)-(32) and (34)

$$\frac{1}{\tau_c(\omega, T)} \approx \frac{5\pi^2}{\alpha} ((\hbar\omega)^2 + (2\pi k_B T)^2) / (1 + \frac{1}{6}(\hbar\omega/\mu)^2 / (1 + 2(k_B T/\mu)^2)). \quad (35)$$

Note that in large range of temperatures the leading contribution to two- electron collision rate

$$\nu_c \equiv \frac{1}{\tau_c(\omega, T)}$$

is defined by the frequency -dependent component of this time. For example, the energies of the dipole Mie resonances in Na clusters are more than 3 eV [8] and value of $(2\pi k_B T)$ at boiling point of the water is approximately equal to 0,2 eV. Therefore the frequency contribution to the collision rate is more than thermal one by a factor of $\sim (3/0.2)^2 \sim 2 \cdot 10^2$.

It should be pointed out that adoption of the relaxation time approximation of form (26) as the collision integral in the kinetic Eq. (2) is formally equivalent (for small damping vibrations) to using of the collisionless Vlasov -Landau equation with finite value of imaginary part of frequency

$$\omega \rightarrow \omega - i\eta, \quad \eta \equiv \frac{1}{\tau_c}. \quad (36)$$

3. Dipole strength distribution for sodium clusters

The strength distribution of the multipole vibrations in a electronic system as a function of the external pressure frequency, see (6), is described by the imaginary part of the collective response function (19). Note that the electron angular momentum λ can be treated either as a continuous or discrete variable [18]. To obtain the collective response function (19) with the electron angular momentum treated as a discrete variable we replace the integration over angular momentum in (20) with sum over discrete values using the semiclassical prescription [32]:

$$\lambda \rightarrow \frac{\hbar}{p_F R} \left(l + \frac{1}{2} \right), \quad (37)$$

and

$$\int_0^1 d\lambda \lambda \rightarrow \left(\frac{\hbar}{p_F R} \right)^2 \sum_{l=0}^{l_{max}} \left(l + \frac{1}{2} \right), \quad (38)$$

where the maximum integer value of electron angular momentum l_{max} is such that $\hbar(l+1/2) < p_F R$. Taking into account eqs.(37) and (38) the function (20) can be written as

$$\begin{aligned} \chi_{int}^L(\omega) = & -\frac{60 \pi}{2L+1} \frac{\omega R}{v_F} \frac{1}{(k_F R)^2} \sum_{N=-L}^L |Y_{LN}\left(\frac{\pi}{2}, \frac{\pi}{2}\right)|^2 \times \\ & \times \sum_{l=0}^{l_{max}} \left(l + \frac{1}{2} \right) \left[1 - l(l+1)/(k_F R)^2 \right] \times \\ & \times ctg \left[\frac{\omega R}{v_F} \sqrt{1 - l(l+1)/(k_F R)^2} - N \arccos \sqrt{l(l+1)/(k_F R)^2} \right]. \end{aligned} \quad (39)$$

Now we apply the presented above approach to the dipole excitations ($L = 1$ in (19),(20)) in spherical sodium clusters. In the calculations the Wigner-Seitz radius r_s was equal to $r_s = 2.25 \text{ \AA}$ [33]. The electron density is

$$\rho_0 = \frac{3}{4\pi r_s^3}. \quad (40)$$

We use the standard formula [20] for the Fermi energy for the alkali

$$\epsilon_F = \frac{p_F^2}{2m} = 50.1 \left(\frac{r_s}{a_0} \right)^{-2} \text{ eV}, \quad (41)$$

where m is electron mass and a_0 is the Bohr radius. The stiffness coefficient of surface displacement Q was chosen to be equal to 10% of the value J given by (5). The dependence of the results on this parameter is rather weak when Q varies in the interval 10% – 30% of the value J . Our results have been obtained by smearing out the δ -functions in the imaginary part of (19) at a finite value of the infinitesimal parameter $\eta = 0.05 \text{ eV}$, see (6). The finite width η simulates some collisional effects. It is equal to the inverse relaxation time if the collision term in eq.(2) was taken into account in a relaxation time approximation, see Sect. 3. The value $\eta = 0.05 \text{ eV}$ corresponds to the value $\sim 10^{-14} \text{ sec}$ for the relaxation time.

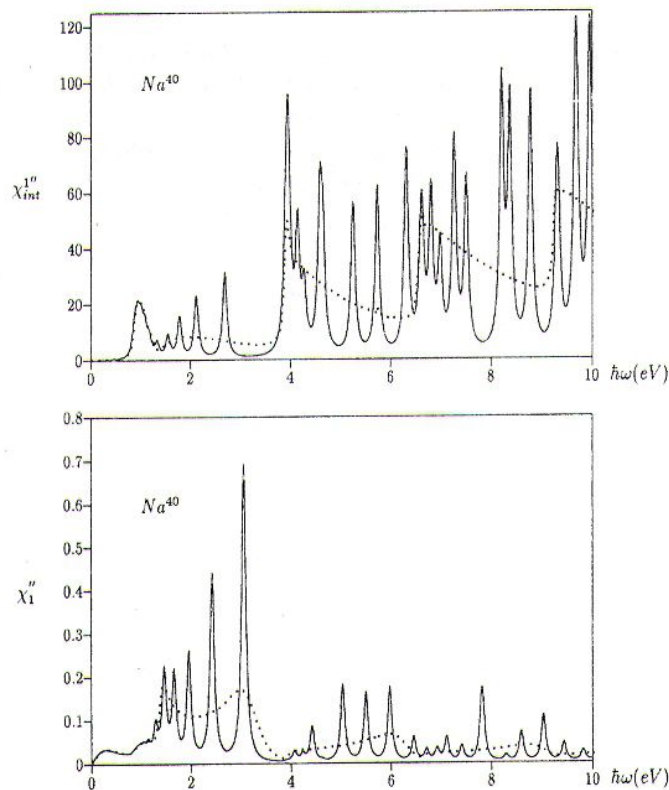


Fig. 1. The imaginary part of the response function for the dipole excitations in the ^{40}Na : a – intrinsic, see (39); b – collective, see (19). The electron angular momentum is treated as discrete variable (solid line) and as continuous one (dotted line). The averaging parameter $\eta = 0.05 \text{ eV}$. The response functions are shown in P_0 units, see text.

First we consider the dipole strength distribution for the ^{40}Na . In Fig.1 the imaginary part of the intrinsic response function (20) (Fig.1a) and the collective one (19) (Fig.1b) are shown. A comparison of Fig.1a and Fig.1b shows that due to the consistency condition (4) one observes the essential strength redistribution. The most of the strength is distributed near the energy of the classical Mie surface plasmon, which lies at $\hbar\omega_M = 3.4\text{eV}$. The centroid of the strength distribution is redshifted with respect to $\hbar\omega_M$. There is the strength distribution in the region of the volume plasmon energy amounted to $\hbar\omega_{pl} = 5.8\text{eV}$. The large fragmentation of the strength is found for the collective dipole excitations. This result is in qualitative agreement with the experimental data [34] for ^{40}Na , which display a broad distribution beginning with 2.4eV .

It might be of interest to study the nature of the dipole excitations in the energy regions where the most of the strength was found. Using Eqs. (19) and (20), we can analyse of the partial contribution of the electron orbits with different angular momentum into the strength function. In Fig.2 the dependence of the energy averaging dipole response function for the ^{40}Na on the electron angular momentum is shown. The energy averaging dipole response function is defined as

$$\langle \chi_1''(l) \rangle = \frac{1}{\omega_1 - \omega_2} \int_{\omega_1}^{\omega_2} d\omega \chi_1''(l, \omega).$$

The maximum integer value of the electron angular momentum for ^{40}Na amounts to $l_{max} = 6$. In Fig.2a we can see that the excitations have rather the surface character in the energy region of the Mie surface plasmon. However the excitations exhibit a certain superposition both the surface mode and the volume one at the energies near the volume plasmon. Note that the results shown in Fig.2 do not depend on the version, in which the electron angular momentum is treated: as a continuous or discrete variable.

Finally in Fig.3 the results are given for the dipole vibrations in the spherical sodium clusters ^{196}Na and ^{440}Na . The increase of the fragmentation is observed as well as the shift of the strength to the low-frequency excitations with increasing of cluster size.

4. Conclusions

We have presented a phase-space approach for the study of multipole collective excitations of the valence electrons in metal clusters within the jellium model. In the case of a gas of valence electrons confined to a sphere with moving surface we have derived the analytical expression for the collective response function, see (19). Introducing the moving effective surface for electronic system in clusters and moreover taking into account the forces which arise at displacement of the electronic surface with respect to the ionic one, see (4), we include in a macroscopic way an electronic interactions in the surface region.

It is found in our semiclassical model that the strength of small spherical metal clusters is localized in two energy regions. Moreover the analysis of the contribution of the electron orbits with different angular momentum into the strength function shows that these two regions are related with the surface and volume branches of the dipole resonance in ^{40}Na , see Fig.2.

The results reflect the fragmentation of the dipole collective strength in clusters due to the coupling both surface and volume collective modes with the single-particle excitations (Landau damping), see Fig.1,3. Found results are in reasonable agreement with the quantum ones obtained recently within the so called generalized vibrating potential model [6].

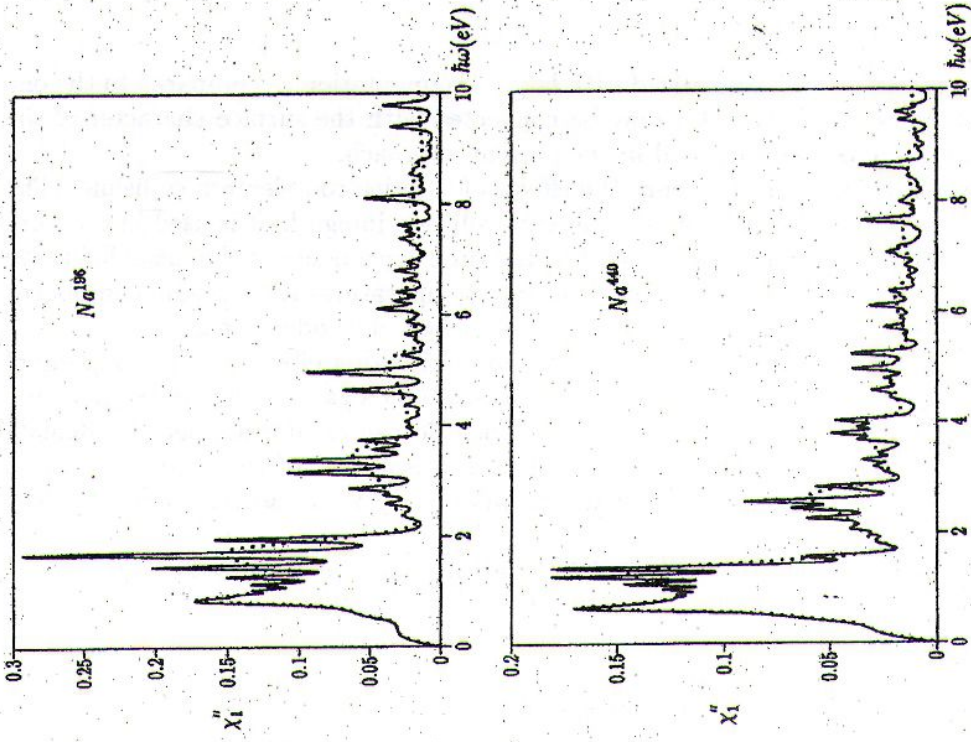


Fig. 3. The imaginary part of the collective response function (19) for the dipole excitations in sodium clusters: a - ^{196}Na ; b - ^{440}Na .

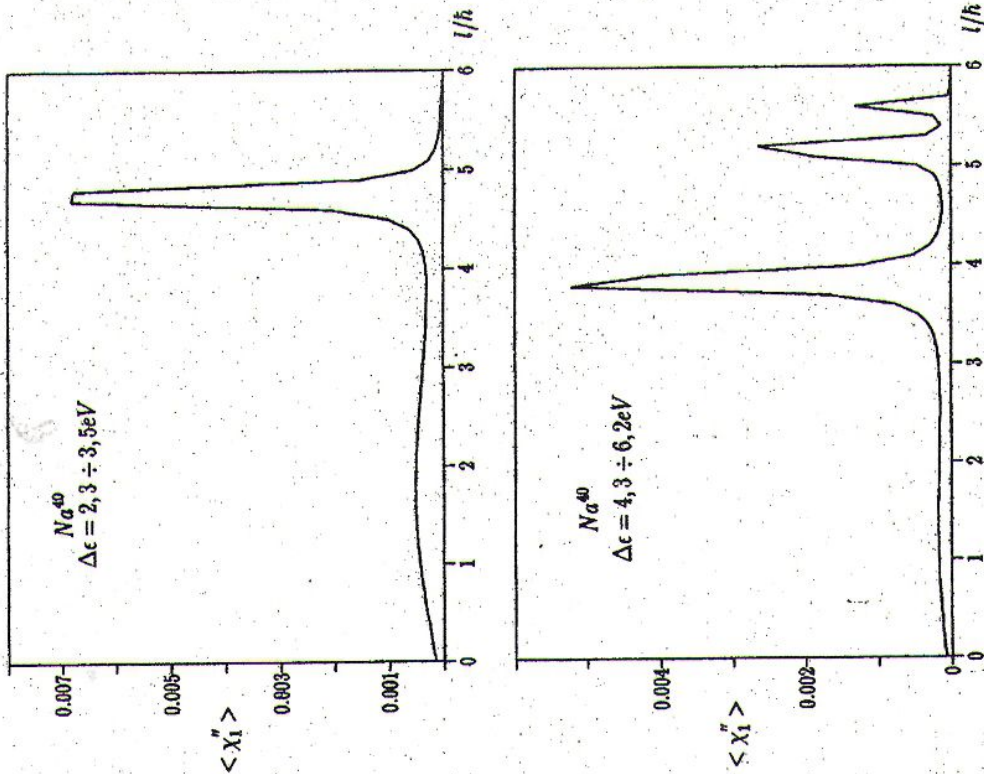


Fig. 2. The dependence of the energy averaging dipole response function for the ^{40}Na on the electron angular momentum. The energy averaging interval: a - $2.3 \leq \hbar\omega \leq 3.5 \text{ eV}$; b - $4.3 \leq \hbar\omega \leq 6.2 \text{ eV}$

Our strength distribution is characterized with larger fragmentation as compared to the one found in the quantum calculations. This may be connected with the surface character of the external pressure form factor, see (6), used in the present approach.

As a first step we have taken into account the effects of the electron-electron collisions. The detail analysis was carried out for the electron-electron collision integral. It is used in the form taking into account the retardation effects caused by the time dependence of the mean field. We shown that for the collective vibrations in large range of temperatures the thermal component of the two- body collision rate is much less than the frequency -dependent one.

The present approach can be modified to account for correlation effects due to coupling of the valence electrons motion to that of the ions as well as to study a gas of non-zero temperature electrons bound by the moving effective surface. This method can be also applied to calculate the dipole strengths in heated and cold Fermi systems for processes of the gamma-decay as well as photoabsorption in a unified way using general relation between radiative strengths and linear response function [36,37].

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ВІДГУК ЕЛЕКТРОННОЇ ПОВЕРХНІ МЕТАЛЕВИХ КЛАСТЕРІВ: ПІДХІД НА ОСНОВІ ДИНАМІКИ У ФАЗОВОМУ ПРОСТОРІ

В.І.Абросімов, В.М.Коломієць, В.А.Плюйко

Вивчаються поверхневі коливання валентних електронів у сферичних алкоїїчних металевих кластерах за допомогою підходу у фазовому просторі, що базується на кінетичному рівнянні Власова — Ландау. Використано теорію лінійного відгуку. Обчислено силову функцію коливань електронної поверхні. Розглянуто дипольні колективні збудження у содових кластерах. Відтворено як поверхневу, так і об'ємну компоненти дипольних збуджень. Аналіз виконано з інтегралом зіткнень між електронами, що враховує ефекти запізнювання. Продемонстровано підвищення швидкості розсіяння електронів при включенні ефектів пам'яті в інтегралі зіткнень.

ОТКЛИК ЭЛЕКТРОННОЙ ПОВЕРХНОСТИ МЕТАЛЛИЧЕСКИХ КЛАСТЕРОВ: ПОДХОД НА ОСНОВЕ ДИНАМИКИ В ФАЗОВОМ ПРОСТРАНСТВЕ

В.И.Абросимов, В.М.Коломиец, В.А.Плюйко

Изучаются поверхностные колебания валентных электронов в сферических щелочных металлических кластерах в рамках динамики в фазовом пространстве, которая основывается на кинетическом уравнении Власова — Ландау. Используется теория линейного отклика. Исследована силовая функция для колебаний электронной поверхности. Рассмотрены дипольные коллективные возбуждения в натриевых кластерах. Получены как поверхностная, так и объёмная компоненты дипольного резонанса. Проведен анализ электрон-электронного интеграла столкновений, который учитывает эффекты запаздывания. Показано, что включение в интеграл столкновений эффектов памяти приводит к усилению скорости электрон-электронного рассеяния.