ELECTRON–PHONON COUPLING AND ANHARMONIC EFFECTS IN METAL CLUSTERS

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Abstract. – The periods of the harmonic oscillations of the ion core of charged sodium clusters around the equilibrium shapes are considered. It is found that these periods are of the order of magnitude of the experimentally measured relaxation times of the plasmons, which suggests the importance of the electron-ion coupling and stresses the role played by the electron-phonon interaction in the dissipation of the plasmon energy. The relation of the process to fission is briefly discussed.

Introduction. – A considerable progress in cluster physics has been achieved for the past years. The picture of the collective motion of the electron system is well understood, [1–3]. The collective electron modes have also been studied experimentally. On the other hand, experiment shows a strong electron-ion correlation, with a characteristic time of $\sim 10^{-12}$ s [4]. There is no complete picture to explain such a strong correlation occurring in spite of the huge difference in the masses which actually justifies the use of the Born-Oppenheimer approximation. In principle, the energy of a plasmon can be directly transferred to the phonons within a time which follows from the analytic solution of a simple model to be presented in greater detail elsewhere,

$$\tau_{pl} = \pi \left( \frac{M}{m} \right)^{\frac{3}{2}} \omega_{pl}^{-1},$$

where $\omega_{pl}$ is the plasmon frequency, $M$ is the mass of the ion and $m$ is the electron mass. For sodium clusters, this time is of the order of $10^{-13}$s, which may be even an order of magnitude shorter than the experiments show. The relaxation time of the plasmon may be identified with $\tau_{pl}$, eq. (1). We summarize now the derivation of eq. (1). We consider plane waves propagating along the z axis. We denote the displacements of the electronic and ionic distributions, respectively, by $u = u(z,t)$ and $v = v(z,t)$. We denote the fluctuations of

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the electronic and ionic charge densities, respectively, by \( \delta \rho_e = e \frac{\partial u}{\partial z} \) and \( \delta \rho_i = -e \frac{\partial v}{\partial z} \). The Lagrangian describing the plasmon–lattice dynamics reads

\[
L = \int dz \left( \frac{1}{2} M \left( \frac{\partial v}{\partial t} \right)^2 + \frac{1}{2} m \left( \frac{\partial u}{\partial t} \right)^2 - \frac{1}{2} \alpha \left( \frac{\partial v}{\partial z} \right)^2 \right) - 4\pi e^2 \int dz \int dz' \left( \frac{\partial u}{\partial z} - \frac{\partial v}{\partial z} \right) |z - z'| \left( \frac{\partial u'}{\partial z'} - \frac{\partial v'}{\partial z'} \right)
\]

where \( u' = u(z') \), \( v' = v(z') \), \( m \) is the electron mass, \( M \) is the ion mass and \( \frac{1}{2} \alpha \left( \frac{\partial v}{\partial z} \right)^2 \) is the elastic energy density of the lattice. The equations of motion read

\[
-M \frac{\partial^2 v}{\partial t^2} + \alpha \frac{\partial^2 v}{\partial z^2} + 4\pi e^2 (u - v) = 0
\]

\[
-m \frac{\partial^2 u}{\partial t^2} + 4\pi e^2 (v - u) = 0.
\]

(2)

It follows that, for an appropriate value of the wave vector, the number of plasmons at time \( t \) is

\[
N_{pl} = uu^* \propto \cos^2 \left( \frac{1}{2} \sqrt{\frac{m}{M}} \omega_{pl} t \right),
\]

so that the plasmon energy will be completely transferred to the lattice in time \( \tau_{pl} \).

Our present purpose is to draw attention to the fact that the periods of the collective vibrations of the ionic core remarkably coincide with the detected electron relaxation times. This fact supports the assumption that the interaction of the electron system with the collective ionic modes plays a rather essential part in dissipation, as, e.g., in the electron-phonon interaction in crystals. There is no need to assume that the phonon excitation will necessarily result into fission, though the two aspects are generically related to one another, so that fission is the ultimate form of a superposition of many of phonons in the limit of large amplitude oscillation [5]. The importance of the collective modes for the electron relaxation was also noted in ref. [6]. The influence of the ionic degrees of freedom on the electronic excitations has been considered in [2, 3, 7].

In turn, cluster fission is a process of great interest. Experiment shows predominance of the strongly asymmetric fission accompanied by emission of mono-, di- or, more rarely, trimers. Symmetric fission remains among the most important topics of research. Study of symmetric fission allows one to better understand the dynamics of the interplay between single-particle and collective degrees of freedom [5].

In paper [8], we have considered the interplay between rotational and vibrational modes of the collective motion in clusters, finally leading to fission. It was specifically found that rotation favors fission through phase transitions occurring in the shape of the clusters rotating with large angular momentum. This is similar to nuclear fission. On the other hand, only neutral clusters were studied in [8]. It is well known, however, that the charge of the clusters plays an important role in fission.

In the present paper we extend our considerations to charged clusters. Moreover, we compare the obtained results with the experimental data, which became available after paper [8] was submitted for publication. Sodium clusters with \( N = 18, 43, 92 \) and 470 atoms are considered. In the light of recent experiments [4], we discuss the role played by the collective motion of the core in the electron-ion correlations. Our discussion is based on the LDM (see [9] and references cited in [5]) which is enough for the present purposes. We take into account surface and Coulomb energies. The inclusion of a shell-correction term generally allows one
to obtain a detailed description of specific features of clusters, such as binding energy per particle, ionization energy etc. [5]. Here, we leave out these aspects, focusing rather on general tendencies than on detailed descriptions of particular properties of individual clusters. On the other hand, the LDM is well-suited for the description of fission, due to its intuitive appeal and transparency. Many properties of nuclear fission have been understood in the framework of the LDM. Representative sodium clusters in a large range of the number \( N \) of the constitutive atoms is dealt with, one of which, \( N = 92 \), is close to the clusters studied experimentally in [4]. We also draw special attention to possible cases of soft clusters with charge close to the critical value, just at the border of Coulomb stability, namely, clusters with \( N = 43, q = 3 \) and \( N = 470, q = 10, q \) being the cluster charge.

Outline of the model. – We consider oscillations of an incompressible liquid drop such that, at each instant, the shape is that of an axially-symmetric spheroid, with time-dependent half-axis \( c \) in the direction \( z \), and time-dependent half-axes \( a = b \) in the perpendicular directions \( x \) and \( y \). We assume irrotational flow. In view of volume conservation, the values of \( c \) and \( b \) are related, at each instant, by \( cb^2 = R^3 \), \( R \) being the radius of the equilibrium spherical shape. For sodium, \( R = 3.93N^{1/3}\text{bohr} \), \( N \) being the number of the atoms in the cluster [12]. We choose \( c \) as the collective variable. The mass parameter can be found by solving the Laplace equation for the velocity field with appropriate boundary condition, analogously to the case of small-amplitude multi-pole vibration [10]:

\[
\Delta \chi(x, y, z) = 0 \quad .
\] (4)

The velocity field is

\[
v(x, y, z) = -\nabla \chi(x, y, z) \quad .
\] (5)

A solution of eq. (4) satisfying the proper boundary condition is

\[
\chi = -\frac{\dot{c}}{4c}(x^2 + y^2 - 2z^2) \quad .
\] (6)

The vibrational kinetic energy can be found as follows:

\[
T = \frac{1}{2} \mu \int (\nabla \chi)^2 dV,
\] (7)

where \( \mu \) denotes the mass per unit volume. From Eq. (6) one gets the expression

\[
T = \frac{1}{2} M(c) \dot{c}^2, \quad M(c) = \frac{1}{5} M(1 + \frac{1}{2}u^3) \quad ,
\] (8)

where \( M \) is the total mass of the cluster, and \( u \) stands for \((R/c)\).

The potential energy of deformation arises from the interplay of the opposite effects of the restoring surface and the repulsive Coulomb energies. For the surface energy, the following expression was derived in [8],

\[
V_{\text{Surf}}(c) = 2\pi \sigma R^2 \left[ u^{-1/2} \text{arcsin} \sqrt{1-u^2} \right] \left[ u^{-1/2} \frac{\text{arcsin} \sqrt{1-u^2}}{\sqrt{1-u^3}} + u \right] - 4\pi \sigma R^2 \quad \text{for} \quad R < c \quad ,
\] (9)

\[
V(c)_{\text{Surf}} = 2\pi \sigma R^2 \left[ u^{-1/2} \text{arcsin} \sqrt{1-u^2} \right] \left[ u^{-1/2} \frac{\text{arcsin} \sqrt{1-u^2}}{\sqrt{1-u^3}} + u \right] - 4\pi \sigma R^2 \quad \text{for} \quad R > c \quad .
\]
where $\sigma$ is the surface tension. For sodium clusters, we take $\sigma = 3.8 \times 10^{-3}$ eV/bohr$^2$ in agreement with the Stabilized Jellium Model [11,12]. The capacities of a prolate spheroid with half axes $c > a = b$ and of an oblate spheroid with half axes $a = b > c$ are [13], respectively,

$$C = \sqrt{c^2 - a^2 \cosh^{-1}(c/a)}, \quad \text{and} \quad C = \sqrt{a^2 - c^2 \cos^{-1}(c/a)}.$$  \hspace{1cm} (10)

These formulae allow us to obtain the Coulomb energy of a charged spheroid,

$$V_{\text{Coul}}(c) = \frac{q^2}{C}. \hspace{1cm} (11)$$

For small deformations the potential energy becomes

$$V^{(2)}(c) = V^{(2)}_{\text{surf}} + V^{(2)}_{\text{Coul}} \hspace{1cm} (12)$$

$$V^{(2)}_{\text{surf}}(c) = \frac{1}{2} k_{\text{surf}} (c - R)^2 \hspace{1cm} (13)$$

$$V^{(2)}_{\text{Coul}}(c) = -\frac{1}{2} k_{\text{Coul}} (c - R)^2, \hspace{1cm} (14)$$

where terms of higher order than the second in $(c - R)$ have been neglected and

$$k_{\text{surf}} = \frac{16\pi \sigma}{5} = 0.0382 eV/a_0^2, \quad k_{\text{Coul}} = \frac{q^2}{N a_0^2 r_s^3} = 0.1794 eV \cdot \frac{q^2}{N a_0^2}. \hspace{1cm} (15)$$

Here, $a_0$ is the Bohr radius, $r_s = 3.93$, the mean radius per particle being $r_s a_0$, and $q = 0, 1, 2, \cdots$ is the charge of the cluster. As in [8], the kinetic energy of the oscillating cluster is

$$T = \frac{1}{2} M(0) \dot{c}^2, \hspace{1cm} (16)$$

where $M(0) = 6.417 \times 10^9 eV N$ and the oscillation period is

$$\tau = 2\pi \sqrt{\frac{M}{k_{\text{surf}} - k_{\text{Coul}}}}. \hspace{1cm} (17)$$

For small amplitudes, our assumptions result in the quadrupole vibrations of a liquid drop. If these assumptions are used in conjunction with different velocity fields from the one considered in the present paper, other types of fission will be favored, as, for instance, asymmetric fission.

Results and discussion. – The results of the calculation are presented in Table I for typical cluster with numbers of atoms $N = 18, 43, 92$ and 470, the charge $q$ being such that the clusters stay within the stability limit.

The periods can be compared with the experimental data [4]. In that paper, characteristic times for the relaxation of the plasmon energy were obtained, which turned out to be $2.5 \times 10^{-12}$ s. As one can see from Table II the plasmon relaxation time is about the same as the characteristic period of the collective vibration. Naturally, for the same period, the plasmon makes thousands of oscillations. The plasmon collective energy is quite likely dissipated by inducing the excitation of the cluster phonons. The electrons collective energy is directly transferred to the ion core, exciting phonon degrees of freedom. In view of the relation $\omega_{\text{ph}} \ll \omega_{\text{pl}}$, the number of excited phonons is very large, $n \gg 1$ [5]. Such many-phonon coherent excitations can then serve as doorway states for fission [15], unless they are destroyed.
by dissipation. The latter process dominates if the spreading width $\Gamma_s$ is greater than the mean spacing of the $n$-phonon states, $\hbar \omega_{ph}$,

$$\Gamma_s \gtrsim \hbar \omega_{ph}. \quad (18)$$

In the case of nuclear fission, the opposite relation to (18), namely, $\Gamma_s \lesssim \hbar \omega_{ph}$, takes place [15]. In this case, the $n$-phonon structure is experimentally observable. This corresponds to the Frenkel picture of fission [14], where the collective deformation arises from a large amplitude oscillation, which, due to an-harmonic effects, never comes back to the initial position, but proceeds towards fission. In this picture, fission occurs on a competitive basis with dissipation of the phonon collective energy inside the ion core. The observed fact that fission most likely occurs through the very asymmetric mode of evaporation of monomers or dimers means that strong dissipation of the core collective motion takes place, and that the relation (18) is satisfied. Moreover, from the expected phonon dissipation time $\tau_{diss} \sim 10^{-12}s$, we can estimate the related spreading width of the $n$-phonon states which turns out to be

$$\Gamma_s^{cl} \sim 7 \times 10^{-4}eV. \quad (19)$$

That is, the many-phonon states strongly overlap. This means that classical approaches, such as the present one, are appropriate for their description.

We note that in some cases, if the cluster is near the border of stability, in so far as $k_{Coul}$ approaches $k_{surf}$, the vibration period increases by an order of magnitude, as for instance in the cases of $\text{Na}_{43}^{3+}$ and $\text{Na}_{470}^{10+}$ in Table I. One can expect that, under these circumstances, the
collective mode can be more easily excited. Experimental study of the electron relaxation and search for near to symmetric fission for such clusters would be of the highest interest.

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