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Anharmonic effects in large-amplitude vibrations of metal clusters

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Abstract. Two types of extreme collective motion, large-amplitude many-phonon vibration of the ionic core and rotation of the cluster with high angular momenta, are considered. The interplay between vibration and collective motion towards fission is discussed. A new mechanism of formation and rupture of the neck is proposed which is based on the Franck-Condon principle, and accounts for the interplay between vibration and fission. Under rotation, the change of the shape of the cluster and a phase transition from axially symmetric to triaxial ellipsoid are predicted. For studying the effects, vibrational motion can be induced by laser radiation. Rotational motion may arise in collisions of clusters.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Ei Phase transitions in clusters

1 Introduction

Much progress has been achieved in understanding of the properties of metal clusters of Na thanks to experimental and theoretical studies undertaken during the last years. Many properties of clusters can be understood in the framework of the Liquid Drop Model (LDM). This model has a firm microscopic basis (*e.g.*, [1–3]), and thus combines merits of relative simplicity and transparency with adequate general description of the phenomena. Sodium clusters are of especial interest. They can be considered as mixed droplets of two kinds of quantal liquids: the ions of the core and the conduction electrons. Due to the difference in masses, each component undergoes its own kind of motion independently, in accordance with the Born-Oppenheimer hypothesis. The electrons perform collective vibrations about the ionic substratum with the plasma frequency. The interplay between these two kinds of motion is analogous to the interplay between the collective and the single-particle modes in nuclei, *e.g.* in fission. The plasmon states can be selectively excited by applying an intense laser field. The plasmon energy can be transferred to the core due to the interaction, leading to fission. Note that, in the case of atoms, the intensity of externally applied resonance radiation of a laser in the vicinity of the nucleus may be considerably enhanced due to resonance properties of the electron shell (*e.g.* [4,5] and references therein). A similar effect may be expected in clusters, where the collective motion of the ionic core towards fission may be induced by laser resonance excitation of the plasmon mode. Understanding the interplay between the different degrees of freedom of the clusters in the dynamics of their laser induced fission is thus a problem of great current interest.

In the present paper we study large amplitude collective motion of the core, preceding fission. At such deformations, certain qualitative and quantitative effects do arise in comparison with small-amplitude collective motion: anharmonicity, three-axiality and others. Our paper is devoted to consideration of these effects.

Our simple estimates based on the liquid-drop model show that the energy $\hbar\omega$ (one quantum of vibration energy) is of the order of 0.001 eV, a value which is several hundred times smaller than a plasmon energy. This is in contrast with nuclear fission, where the excitation of 8–10 low-lying quadrupole phonons is enough to reach the fission barrier (*e.g.* [6] and references cited therein). For this reason, a large-amplitude vibration of the core leading to fission inevitably contains a great number of elementary phonons and, therefore, can be described classically.

In Section 2 we consider classical vibrations of a quantal liquid droplet undergoing ellipsoidal deformations in the framework of the LDM, assuming irrotational flow of an incompressible liquid. The conclusions of this pedagogical calculation lead to the development of useful insights into the physics of fission. The analytical solutions obtained in Section 2 confirm the validity of the Werner-Wheeler method which is used to describe fission within the LDM. Furthermore, the present analysis allows one to look at the formation and rupture of the neck from another angle. There is an open question of the mechanism of the neck rupture: fluctuation of density, random neck rupture, etc. Depending on the approach, various forms and thicknesses of the neck are considered. Ellipsoidal

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deformation with large amplitude which is considered in Section 2 should finally go into the fission mode which is characterized by another shape, *e.g.*, that of two intersecting spheres. In Section 3 we propose a new mechanism for the transition between the two families of shapes which is in fact founded on the Franck-Condon principle and accounts for the interplay between vibration and fission. Numerical results, including the density of vibrational levels, are also presented in Section 3. In Section 4 we outline a possible approach to the description of the interaction between the plasma-type excitations and the motion of the ionic core. In Sections 5 and 6, the rotation of a cluster with a certain angular momentum is considered.

In conclusion, we sum up the results and outline the perspectives for future investigations.

2 Ellipsoidal shape parameterization

Let us consider a vibration of an incompressible liquid drop such that, at each instant, the shape is an ellipsoid, with time-dependent half-axis c in the direction z, and time-dependent half-axis 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 the equality $cb^2 = R^3$, R being the radius of the drop with an equilibrium spherical shape: $R = 3.93N^{1/3}$ bohr, N being the number of the atoms in the cluster [7]. Choose c as a collective variable. Then the mass and restoring force parameters can be found by solving the Laplace equation for the velocity field with appropriate boundary condition, analogously to the case of small-amplitude multipole vibration [8]:

$$\Delta\chi(x,y,z) = 0. \tag{1}$$

The velocity field is given by

$$\mathbf{v}(x,y,z) = -\boldsymbol{\nabla}\chi(x,y,z). \tag{2}$$

Hereafter we use the notation $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ for the unit vectors along the Cartesian axes x, y and z, respectively. A solution of equation (1) satisfying the proper boundary condition is given by

$$\dot{\mathbf{r}}(t) \equiv \mathbf{v}(t) = \frac{\dot{c}}{2c}\left(x\hat{\mathbf{i}} + y\hat{\mathbf{j}} - 2z\hat{\mathbf{k}}\right). \tag{3}$$

Indeed, if we define the surface by $F(\mathbf{r},t) = 0$, where

$$F(\mathbf{r},t) \equiv \frac{x^2}{a^2(t)} + \frac{y^2}{b^2(t)} + \frac{z^2}{c^2(t)} - 1, \quad \text{with } a = b, \tag{4}$$

then the surface condition [9,10]

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \dot{\mathbf{r}} \cdot \boldsymbol{\nabla}F + \frac{\partial F}{\partial t} = 0, \tag{5}$$

with allowance for equation (3) and volume conservation, is fulfilled.

Solution (3) illustrates the Werner-Wheeler method which found its application in fission of nuclei (*e.g.* [10–13]). In this method, irrotational flow in fission can be considered as a flow of circular layers of liquid. Moreover, every disc changes with time its thickness and radius, but remains a disc. Indeed, according to equation (3), the local velocity turns out to be a linear function of the Cartesian coordinates of the point x, y, z. Thus, for every coordinate z, the z component of the velocity is independent of x and y. This fact proves the Wheeler's suggestion in the case of an ellipsoid. The translational velocity of the c.m. of a slice perpendicular to the symmetry axis is proportional to z.

The vibrational kinetic energy can be found as follows:

$$T = \frac{1}{2}\mu\int(\boldsymbol{\nabla}\chi)^2\mathrm{d}V = \frac{1}{2}\mu\oint\chi(\boldsymbol{\nabla}\chi)\cdot\hat{\mathbf{n}}\,\mathrm{d}S, \tag{6}$$

where μ denotes the mass per unit volume, $\hat{\mathbf{n}}$ is the unit normal vector at the surface and $\mathrm{d}S$ is the element of surface area. From equation (3) one gets the expression

$$T = \frac{1}{2}\mathcal{M}(c)\dot{c}^2 \tag{7}$$

with the variable mass parameter

$$\mathcal{M}(c) = \frac{1}{5}M\left(1 + \frac{1}{2}u^3\right), \tag{8}$$

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

The potential energy is given by

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

$$V(c) = 2\pi\sigma R^2\left[u^{-1/2}\frac{\mathrm{arcsh}\sqrt{u^3-1}}{\sqrt{u^3-1}} + u\right] - 4\pi\sigma R^2 \quad \text{for} \quad R > c,$$

where σ is the surface tension. For sodium clusters, we use a value of 3.8×10^{-3} eV/bohr^2 for σ, obtained within the Stabilized Jellium Model [7]. For small amplitudes, equation (9) reduces to the form of a harmonic oscillator potential energy

$$V(c) = \frac{8\pi\sigma}{5}(c-R)^2. \tag{10}$$

Relativistic units $\hbar = c = 1$, are used throughout the paper. From equations (7, 8, 10), it follows that, for small amplitudes ($u \sim 1$), the system undergoes harmonic motion with the oscillation frequency

$$\Omega = \frac{\omega_0}{\sqrt{N}}, \tag{11}$$

$$\omega_0 = 4\sqrt{\frac{2\pi\sigma}{3m}} \approx 9\times10^{-3}\ \text{eV}, \tag{12}$$

m being the mass of a Na atom, in accordance with what was said in the introduction. The period of the anharmonic vibration is given by

$$\tau = 2\int_{c_1}^{c_2} \sqrt{\frac{\mathcal{M}(c)}{2(E-V(c))}}\mathrm{d}c, \tag{13}$$

where c_1 and c_2 are, respectively, the minimum and maximum value of the semi-axis in the z-direction. Here, E is the total energy, kinetic energy (6) plus potential energy (9). It will be seen that the period τ is a strongly increasing function of E. The density of the levels for the present vibration can be calculated by means of the formula

$$\frac{\mathrm{d}n}{\mathrm{d}E} = \frac{1}{2\pi}\frac{\mathrm{d}(E\,\tau)}{\mathrm{d}E}. \tag{14}$$

Since τ increases rather steeply with E, also $\mathrm{d}n/\mathrm{d}E$ is a steep function of E. This may be the source of an important damping mechanism of the plasmon mode through a decay into many large amplitude vibrational modes, as discussed below.

About the same separation of the vibration levels was found in reference [14] within the model of irrotational incompressible classical liquid drop. This spacing is by two to three orders of magnitude smaller than the fission barrier in symmetric fission. Such a high density shows that the collective motion of the ion substratum towards fission can be treated classically. This aspect is discussed in detail with respect to ternary fission in reference [14]. We shall return to its discussion below in the next section.

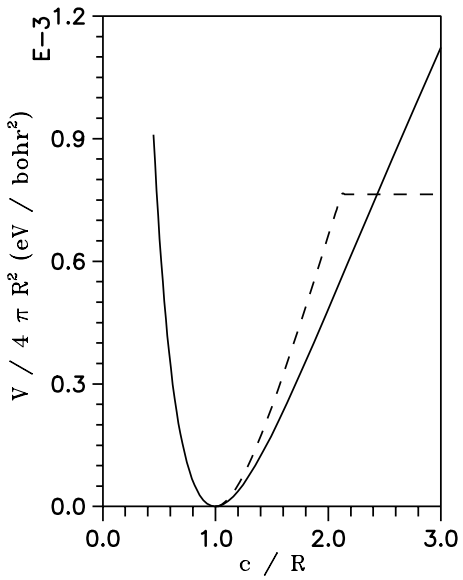

Fig. 1. The potential energy of an ellipsoid of revolution, $V(c)/4\pi R^2$ *versus* c/R, is shown by the full line and is compared with the potential energy, represented by the dashed line, of a cluster with the shape of two intersecting spheres. The distance between the centers of mass of the spheres is the same as the distance between the centers of mass of the two halves into which the ellipsoidal shape is divided by a plane perpendicular to its axis.

3 Necking mechanism

In Figure 1 we present the deformation energy calculated by means of equation (9) divided by $4\pi R^2$. This is a universal function for all the clusters, independent of the number of constituent atoms. The anharmonic effects strongly manifest themselves already for vibration amplitudes such that $(c-R)/R \geq 0.05$.

How this kind of collective motion can lead to a fission mode is an interesting question. Symmetrical fission of sodium clusters was never observed in experiment, while in many theoretical papers deformation energy and saddle shapes are studied. To discuss this question, we also consider another kind of deformed shape which finally leads to fission, as two intersecting spheres. Consider the deformation of a neutral cluster. The corresponding potential energy of deformation is also plotted in Figure 1. At first the spheres intersect each other, but, eventually, will separate. The radii of the spheres are such that the total volume remains constant, and the distance between their centers of mass (which do not coincide with the geometrical centers when the spheres actually intersect each other) is the same as the distance between the centers of mass of the two halves into which the ellipsoidal shape is divided by a plane perpendicular to its axis. Only the free surface of the spheres contributes to the potential energy. As one can see, the second curve lies higher, up to the point of scission, which corresponds to two spheres in contact. But, after scission, further motion of the separated fragments does not cause any change of the potential energy. Due to this circumstance, at some point R_{cr} the curves cross each other. Further deformation of an ellipsoidal cluster needs more energy than the motion of the separated fragments. The dynamics of the transition between the two families of deformation involves a mechanism of barrier penetration. This concerns the very interplay between quantum and classical mechanics, illustrating quantitative change of the properties with the size of the system. The Coulomb force for charged clusters favours deformation towards fission. The same applies to shell effects for proper systems [14]. It seems however that neither of these reasons can explain clearly the penetration mechanism. Moreover, symmetric fission has not been observed yet, even in charged clusters. It seems that the presence of the relevant degree of freedom is more strongly felt in small Fermi systems. With increasing size of the system, this degree of freedom is dissolved in the thermostat of many single-particle degrees of freedom, and is thus merely lost due to negligible statistical weight. This question shall be considered elsewhere, in finer detail. Note that, in the case of nuclei, a barrier related to the necking was first considered in reference [15].

In Figure 2, the period, divided by $N^{1/2}$, is plotted as a function of the vibration energy divided by $N^{2/3}$. Again, a universal function, independent of the numbers of constituent atoms, is found. The periods divided by $N^{1/2}$ explicitly display the anharmonic effects, strongly deviating from the small amplitude behaviour, equation (11).

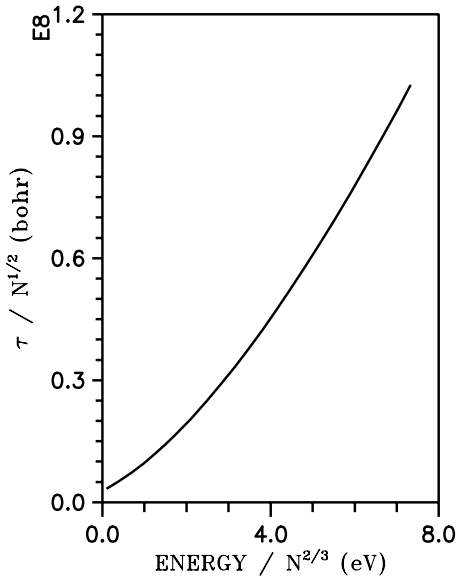

Fig. 2. The period τ scaled by $N^{1/2}$ *versus* the vibrational energy E scaled by $N^{2/3}$.

The periods are close to one another for very small vibration amplitudes, but diverge with the amplitude, when it becomes large. For pure harmonic vibrations, the period scaled with $N^{1/2}$ is constant for all the energies and numbers of the constituent clusters. A very large period associated with a large amplitude oscillation implies that the cluster will be strongly deformed long enough to allow for the rearrangement of its particles into two separate cluster to occur.

In conclusion, we may expect that a plasmon will decay by exciting a large amplitude highly anharmonic oscillation, but it may also decay by exciting a very short wavelength harmonic oscillation of the ionic substratum.

4 Damping of plasmon

The interaction potential between the electronic charge density fluctuation $\rho_{\rm e}(\mathbf{r})$ and the ionic charge density fluctuation $\rho_{\rm I}(\mathbf{R})$ is written

$$H' = -e^2 \int \mathrm{d}^3 r\, \mathrm{d}^3 R\, \frac{\rho_{\rm e}(\mathbf{r})\rho_{\rm I}(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|} \sim -e^2 \int \mathrm{d}^3 r\, \mathrm{d}^3 R\, \frac{r_<^l}{r_>^{l+1}} \rho_e(\mathbf{r}) Y_{lm}^*(\hat{r}) Y_{lm}(\hat{R}) \rho_{\rm I}(\mathbf{R}). \quad (15)$$

This interaction gives rise to a coupling between the plasma oscillations and the vibrations of the ionic substratum. Due to resonance effects, this coupling may become relevant for large wave vectors. The interaction (15) can induce the development of collective flow towards fission. For $l = 1$ fluctuations this effect may be related to the center of mass motion, but already for $l = 2$ fluctuations the appearance of such a collective mode seems possible.

Effectively, let q denote the amplitude of the electronic density oscillations associated with the plasmon mode in the cluster and ω the plasmon frequency, so that the plasmon Hamiltonian is $H_{\rm pl} = p^2/2 + \omega^2 q^2/2$. Denote by Ω the frequency of the cluster shape oscillations and by Q the corresponding amplitude, so that $H_{\rm ph} = P^2/2 + \Omega^2 Q^2/2$ is the Hamiltonian describing the shape oscillations. For small q, Q the deformation energy of the cluster is $V(q,Q) = \omega^2 q^2/2 + \Omega^2 Q^2/2$. However, Q may easily become large, since the cluster is soft against shape fluctuations, so that $V(q,Q)$ should not be expanded in powers of Q. The relevant physical processes are not harmonic in Q. The elastic energy $\Omega^2 Q^2/2$ should itself be replaced by a potential $V_1(Q)$ and $V(q,Q)$ should be expanded as $V(q,Q) = \omega^2 q^2/2 + V_1(Q) + qV_2(Q)$. Since the plasmon frequency is essentially independent of the shape of the cluster, we assume ω to be independent of Q. This mechanism leads to a strongly anharmonic coupling between the plasmon degree of freedom and the degree of freedom associated with the ions, such as the following model Hamiltonian describes

$$H = \omega a^\dagger a + \Omega b^\dagger b + g\left(a^\dagger {b^\dagger}^n + {b^\dagger}^n a\right). \quad (16)$$

Since the plasmon is expected to decay into a large amplitude vibrational state of the ionic substratum with the same energy, we assume that $\omega = n\Omega$. Let

$$|\Phi\rangle = \alpha(t) a^\dagger |0\rangle + \beta(t) \frac{{b^\dagger}^n}{\sqrt{n!}} |0\rangle \quad (17)$$

represent the state of the cluster at time t. The time evolution of the amplitudes α, β is determined by the Lagrangian $L = \mathrm{i}\langle\Phi|\dot{\Phi}\rangle - \langle\Phi|H|\Phi\rangle$. We find $L = \mathrm{i}(\alpha^*\dot{\alpha} + \beta^*\dot{\beta}) - (\omega(\alpha^*\alpha + \beta^*\beta) + G(\alpha^*\beta + \alpha\beta^*))$, where $G = \sqrt{n!}g$, so that

$$\mathrm{i}\dot{\alpha} = \omega\alpha + G\beta, \quad \mathrm{i}\dot{\beta} = \omega\beta + G\alpha. \quad (18)$$

If at time $t = 0$ the cluster supports a plasma oscillation so that $\alpha(t) = \alpha_0,\ \beta(t) = 0$, then at time t we have

$$\alpha(t) = \frac{\alpha_0}{2} \exp(-\mathrm{i}\omega t)(\exp(-\mathrm{i}Gt) + \exp(\mathrm{i}Gt)). \quad (19)$$

On the other hand

$$\beta(t) = \frac{\alpha_0}{2} \exp(-\mathrm{i}\omega t)(\exp(-\mathrm{i}Gt) - \exp(\mathrm{i}Gt)). \quad (20)$$

On physical grounds we expect that $\omega \gg g$. However, the anharmonicity enhances the coupling by a factor $\sqrt{n!}$. As a result of this mechanism, energy is transferred from the plasmon to the ionic degrees of freedom.

5 Rotational motion

Rotational motion of a classic liquid drop has been considered within certain models *e.g.* in references [16,17] and other papers cited therein. The shape of the rotating drop was restricted to a symmetric ellipsoid. In the case of clusters, however, triaxial shapes have been observed [18]. It is, therefore, reasonable to abandon the above restriction.

Let us consider the deformation of a spherical cluster subject to rotational motion in finer detail [19]. We shall also consider the influence of such a motion on the stability of the cluster with respect to the phase transition from the oblate biaxial to the triaxial form. Assuming rotation around the x-axis, the energy functional is

$$\mathcal{W}[x(\rho),\omega(\rho)] = \sigma 4\pi \int \mathrm{d}\rho\, \rho\sqrt{1+x'^2} + \frac{1}{2}4\pi\mu \int \mathrm{d}\rho\, \omega^2\rho^3 x - \lambda 4\pi \int \mathrm{d}\rho\, \rho x - \lambda' 4\pi\mu \int \mathrm{d}\rho\, \omega\rho^3 x\,, \quad (21)$$

where λ and λ' denote Lagrange multipliers fixing the volume and the angular momentum. Here, ω is the angular velocity, $\rho = \sqrt{z^2+y^2}$, the shape of the cluster is specified by $x(\rho)$, $x' = \mathrm{d}x/\mathrm{d}\rho$, and μ is the mass density. This functional represents the energy in the lab system with a constraint on the angular momentum.

Varying the functional (21) with respect to ω, one finds the relation

$$\lambda' = \omega, \quad (22)$$

from where it follows, in particular, that ω is constant with respect to ρ.

Substituting equation (22) into equation (21), one obtains the following functional to minimize:

$$\mathcal{W}[x(\rho)] = \sigma 4\pi \int \mathrm{d}\,\rho\, \rho\sqrt{1+x'^2} - \lambda 4\pi \int \mathrm{d}\rho\, \rho x - \frac{1}{2}\omega^2 4\pi\mu \int \mathrm{d}\rho\, \rho^3 x. \quad (23)$$

This functional represents the energy in the intrinsic reference system. The Euler Lagrange equation defining the deformation of the cluster is

$$\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\rho\frac{x'}{\sqrt{1+x'^2}}\right) + \frac{\lambda}{\sigma}\rho + \frac{\omega^2\mu}{2\sigma}\rho^3 = 0. \quad (24)$$

By integration we obtain

$$\frac{x'}{\sqrt{1+x'^2}} + \frac{\lambda}{2\sigma}\rho + \frac{\omega^2\mu}{8\sigma}\rho^3 = 0. \quad (25)$$

The integration constant is fixed by the requirement $x'(0) = 0$. Thus, for small ω,

$$x' = \frac{\eta\rho}{\sqrt{1-\eta^2\rho^2}}\left(1+\gamma\frac{\eta^2\rho^2}{1-\eta^2\rho^2}\right), \quad (26)$$

where $\eta = \lambda/(2\sigma)$, $\gamma = \omega^2\mu\sigma^2/\lambda^3$. Integrating again, we obtain

$$\frac{x^2}{1-4\gamma} + \frac{\rho^2}{1-2\gamma} = \frac{4\sigma^2}{\lambda^2}\cdot \quad (27)$$

From volume conservation, it follows $\lambda^2 = \lambda_0^2\,(1-8\gamma/3)$. Thus, with $\gamma_0 = \omega^2\mu\sigma^2/\lambda_0^3$,

$$\frac{x^2}{1-\frac{4}{3}\gamma_0} + \frac{\rho^2}{1+\frac{2}{3}\gamma_0} = \frac{4\sigma^2}{\lambda_0^2}\cdot \quad (28)$$

If the droplet undergoes a vibrational motion superimposed on a rotational motion, the velocity field may be decomposed into a field describing a pure rotational motion and a field describing an irrotational flow, such as

$$\mathbf{v} = \omega\left(z\hat{\mathbf{j}} - y\hat{\mathbf{k}}\right) + q\left(x\hat{\mathbf{i}} + y\hat{\mathbf{j}} - 2z\hat{\mathbf{k}}\right), \quad (29)$$

for, let us say, $t = 0$. Both the spring constant and the mass parameter of the vibration are affected by the rotation. Depending on the value of the angular velocity ω, the spring constant may become negative due to centrifugal stretching, indicating the tendency to fission.

Thus, the shape undergoes a phase transition. Let us consider the process in finer detail. Regarding a triaxial ellipsoid, the term corresponding to the kinetic energy (and representing the centrifugal potential with the minus sign) can be obtained as

$$T = \frac{1}{10}\omega^2 M(b^2+c^2) = \frac{5L^2}{2M(b^2+c^2)}, \quad (30)$$

where M is the mass of the cluster. In obtaining equation (30), we took into account the relation between the angular momentum and the angular velocity

$$\omega = \frac{5L}{M(b^2+c^2)}, \quad (31)$$

which can be obtained by differentiating the first expression in (30) with respect to ω.

Therefore, for fixed L, the kinetic energy term (30) decreases with the deformation, decreasing thus the energy functional. The gain is proportional to L^2. On the other hand, the deformation increases the surface energy. For a triaxial ellipsoid, the latter has a general form

$$S = \frac{3V}{2\pi a}\int_0^{2\pi}\mathrm{d}\phi \int_0^1 \frac{r\,\mathrm{d}r}{\sqrt{1-r^2}} \times\sqrt{1-r^2+\left(\frac{a}{b}r\cos\phi\right)^2+\left(\frac{a}{c}r\sin\phi\right)^2}. \quad (32)$$

If ω is not high, equation (32) can be expanded in a Taylor series with respect to a small deformation parameter δ:

$$b = r_0\left(1-\delta+\frac{1}{2}\delta^2\right), \quad c = r_0\left(1+\delta+\frac{1}{2}\delta^2\right). \quad (33)$$

Substituting equation (33) into equation (32), one finds that the first non vanishing δ-dependent term is of second order in δ:

$$S = \frac{3V}{r_0}\int_0^1 \frac{r\,\mathrm{d}r}{\sqrt{1-r^2}}\sqrt{p}\left[1+\frac{r^2}{p}\left(1-\frac{r^2}{4p}\right)\delta^2\right], \quad (34)$$

where

$$p(r) = \kappa^2 + r^2\left(1-\kappa^2\right).$$

with

$$\kappa = \frac{r_0}{a} = \frac{r_0^3}{R^3}\cdot$$

The value of r_0 is determined by minimizing, for fixed ω, $\mathcal{E}' = U_{\rm c.f.}(r_0) + V(r_0)$, where $U_{\rm c.f.}(r_0) = -T$ and $V(r_0) = V(a)$, according to the second of equations (9), with $u = r_0^2/R^2 = R/a$. We observe that $\mathcal{E}'$ is not the true energy. It is the energy in the intrinsic system, but, in the lab system it actually represents the Lagrangian since $U_{\rm c.f.}(r_0) = -T$, where $T = \omega^2 M r_0^2/5 = 5L^2/(4Mr_0^2)$ is the kinetic energy. The true energy, in the lab system, is $\mathcal{E} = 5L^2/(4Mr_0^2) + V(r_0)$. Minimizing $\mathcal{E}$ for fixed angular momentum L is the same as minimizing $\mathcal{E}'$ for fixed ω. It is easily verified that, for sodium clusters, there is an asymptotic value for the angular velocity, $\omega = 0.96\Omega$, with Ω defined in (11), for which $\mathcal{E}$ goes to infinity.

Next, we consider the effect of rotation on a cluster with a small instantaneous triaxial deformation due to vibrational motion. In particular, we focus on the spring constant for triaxial deformation,

$$\mathcal{K} = 2\sigma \frac{3V}{r_0} \int_0^1 \frac{r\,{\rm d}r}{\sqrt{1-r^2}} \frac{r^2}{\sqrt{p}} \left(1 - \frac{1}{4}\frac{r^2}{p}\right) - \frac{4}{5} M r_0^2 \omega^2. \quad (35)$$

There is a negative contribution to the spring constant, which physically comes from the term of the centrifugal potential, and a positive contribution arising from the surface tension. Which one of the two contributions dominates depends on the value of r_0/R. This value is, in turn, ruled by the value of the frequency ω.

6 Numerical results for rotation

We find that $\mathcal{K}$ given by equation (35) becomes negative for

$$\omega_{\rm c} = 0.56\Omega, \quad (r_0)_{\rm c} = 1.13R, \quad L_{\rm c} = 0.72L_0, \qquad (36)$$

where $L_0 = 2MR^2\Omega/5$, is the angular momentum of a spherical cluster with the same volume, rotating with frequency (11). We remark that all the above critical quantities scale with powers of N, *e.g.* $\hbar\omega_{\rm c} = 5.1 \times 10^{-3} N^{-1}$ eV, $(r_0)_{\rm c} = 4.44\, N^{-1/3}$ bohr, $L_{\rm c} = 62.3 N^{7/6}\hbar$. Furthermore, the critical value of the dimensionless quantity

$$y = \frac{5}{16\pi} \frac{L^2}{MR^4\sigma}.$$

is $y_{\rm c} = 0.593$. Further details on the behavior of the "overcritical" system depend mainly on whether the angular velocity ω is considered as the basic variable parameter, or the angular momentum L. If ω is varied, there is a rather abrupt change of shape for $\omega > \omega_{\rm c}$. This is due to the centrifugal acceleration which further stretches the optimal shape of the cluster. The behaviour of the rotating cluster is illustrated in Figure 3. A plot of the energy $\mathcal{E}$ of the rotating cluster *versus* ω, for the axial symmetric shape, is shown in Figure 3a. For values of ω above the critical value, the curve represents a metastable state. We also observe that the cluster does not support higher angular velocities than a specific maximum. If, artificially, a higher angular velocity than that maximum is imposed, the cluster unavoidably disintegrates. In Figure 3b, the energy is presented as a function of L, again for the axial symmetric shape. Comparison of Figures 3a and 3b shows that the angular velocity is not an adequate dynamical variable at critical values of L. This is in contrast *e.g.* with the cranking model widely used in nuclear physics. Further increase of the angular momentum, or the kinetic energy of rotation, occurs approximately without change of the angular velocity ω. That mainly causes further elongation of the shape of the rotating cluster. Approximately linear

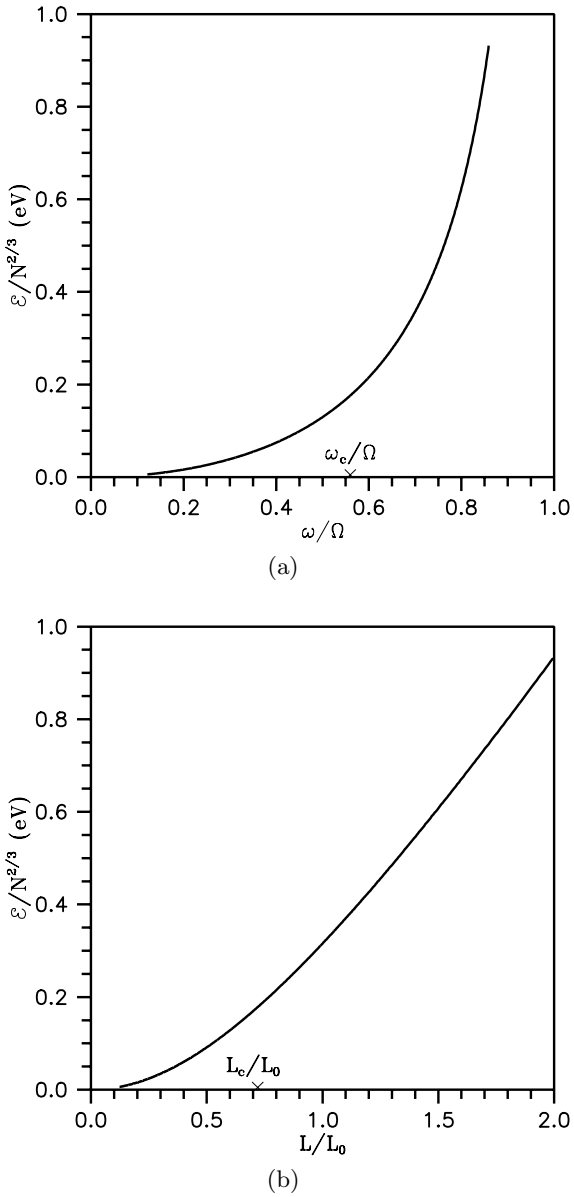

Fig. 3. The total energy of the rotating cluster $\mathcal{E}$ *versus* the frequency ω scaled by Ω (see Eq. (15)), is shown in (a). In (b), the same quantity is shown *versus* the angular momentum L scaled by L_0 (the angular momentum of the corresponding spherical cluster).

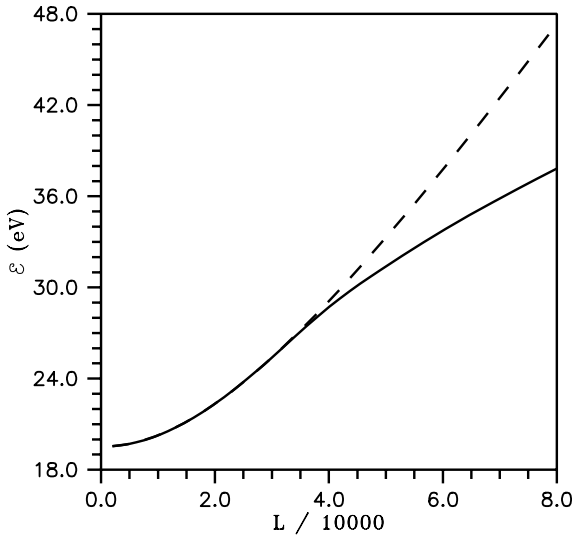

Fig. 4. Total energy $\mathcal{E}$ of a 200-atom rotating sodium cluster *versus* the angular momentum L for the axial symmetric shape (dashed line) and the triaxial shape (full line).

Table 1. Change of the ellipsoidal shape of a rotating cluster with the a, b and c the half-axes in the point of the phase transition.

E, eV	a, bohr	b, bohr	c, bohr
$N = 24$, $R = 11.34$ bohr			
6.537	7.95	13.54	13.54
6.543	7.85	11.09	16.72
$N = 50$, $R = 14.48$ bohr			
10.66	10.2	17.3	17.3
10.67	10.0	14.2	21.3
$N = 100$, $R = 18.2$ bohr			
16.81	12.88	21.70	21.7
17.31	12.3	16.4	30.0
$N = 300$, $R = 26.3$ bohr			
35.2172	18.4	31.4	31.4
35.2178	18.2	25.9	38.6
$N = 500$, $R = 31.2$ bohr			
49.51	21.9	37.2	37.2
49.60	21.9	30.6	45.4

dependence of $\mathcal{E}$ on L for $L \gg L_c$ in Figure 3b shows that rotation at overcritical angular momenta occurs with constant ω.

Furthermore, we have minimized, with respect to b and c, the full energy for different values of L around the critical value. In Figure 4 we present the full energy as a function of L for the axial symmetric and the triaxial shape, for a sodium cluster with $N = 200$. It can be seen that a phase transition occurs at $L \approx 4 \times 10^4 \hbar$.

We note with equation (36) that the critical energy and momentum increase with the number of atoms in the cluster as $N^{2/3}$. In Table 1 we present the change of the half-axes of the clusters due to the rotation energy. One can conclude from those results that a phase transition of the first kind takes place, when the shape of the cluster abruptly changes at the critical point. Note that the half-axis which is in the direction of the rotation momentum remains practically unaffected by the phase transition. The change of shape occurs in the plane perpendicular to the rotation axis, from a circular to an elliptic form, in accordance with what is said above.

The kinetic energies of rotation at the critical point of the phase transition E_c turn out to be in the eV to tens-eV energy domain. Such energies look very accessible and may be realized in experiment by merging of colliding clusters. The change of the shape can be detected in experiment in the same ways as in the case of nuclei, *e.g.* by splitting of the GDR.

7 Conclusion

We now summarize the results and outline perspectives for further investigation.

In the present paper we have studied some questions connected with the vibrational and rotational motions of the ionic core arising in an excited sodium cluster, and their relation to the collective motion towards fission. First, we would like to stress that the effects considered arise at energies of tens eV, which can be realized in experiment *e.g.* in collisions of clusters. Our consideration is based on the LDM. One might expect the appearance of certain peculiarities due to the shell effects. The latter effects, however, should not affect essentially the general picture presented previously, and may be considered in a separate paper. The same applies to the Coulomb effects arising when ionization processes take place, which also occur in the collisions.

The main results obtained above can be summarized as follows.

(1) Anharmonic effects are considered which essentially influence the energy spacing and period of the large-amplitude vibration. These effects are important, specifically, for the coupling between the ionic and electronic motion.
(2) Change of the shape, which arises on account of the rotation of the cluster with large angular momentum, is also considered. The results obtained may be also of interest for nuclear physics (*e.g.*, for the cranking model). For relatively small angular velocities, the results are obtained analytically. For arbitrary velocities, a phase transition takes place to the triaxial shape. These effects could be observed in experiment *via* splitting of the giant multipole resonances.
(3) A new mechanism of necking is suggested based on the Frank-Condon principle.

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