

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 40, NUMBER 5

15 AUGUST 1989-I

Thermal line broadening in small metal clusters

G. F. Bertsch and D. Tománek

*Department of Physics and Astronomy, Cyclotron Laboratory, and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824-1116*

(Received 15 February 1989)

Plasmon broadening in small metal clusters is calculated using the jellium model. We find that thermal fluctuations in the shape of the cluster could be a significant source of broadening of the Mie resonance. The shape fluctuation mechanism makes definite predictions for the shape of the resonance line, its temperature dependence, and its dependence on cluster size.

Recent experiments have observed the surface-plasmon resonance in small sodium clusters.^{1,2} The in-flight experiment¹ on 2–40-atom Na clusters found the plasmon frequency to lie at ≈ 2.5 eV and the corresponding linewidth of ≈ 0.4 eV. Very similar parameters were observed in very large clusters of about 100–1500 Å deposited on a substrate.² In this paper, we offer the first quantitative calculation of the plasmon linewidth of these clusters. Unlike in all available cluster calculations, which are based on the Born-Oppenheimer approximation, we explicitly consider the influence of atomic vibrations on the broadening of the plasmon resonance. We find that this is the dominant line broadening mechanism in very small clusters such as Na₂₀, as previously suggested by de Heer.¹

The best-founded theory of plasmon excitations is the random-phase approximation (RPA),³ which predicts resonance frequencies close to the classical Mie frequency.⁴ Contrary to the experiment, the RPA resonance line is very narrow³ in small clusters for the following reason. The RPA excitation is a one-particle, one-hole excitation which can mix with more complicated electronic configurations beginning with two-particle, two-hole. These may be important in larger system, but their level density is too low to make them significant in the clusters we consider. We estimate⁵ that in Na₂₀ the gap between occupied and unoccupied electron states is ≈ 1 eV. It thus requires at least 2 eV to make a two-particle, two-hole state. When we also require that the quantum numbers of the Mie plasmon be conserved, the energy of the lowest two-particle, two-hole state is higher than 3 eV. Thus the observed resonance at 2.5 eV will not mix noticeably with these higher electronic excitations and hence will lead to a negligible linewidth. Similarly, the contribution to the linewidth due to direct plasmon decay can be neglected. The only significant line broadening

mechanism is the coupling of plasmons to cluster vibrations, which in the jellium model are due to the shape changes of the jellium background. A similar mechanism has been suggested in nuclear physics to describe the thermal broadening of nuclear collective excitations.⁶ We shall consider as a particular example the $N=20$ sodium cluster, which was studied experimentally in Ref. 1. In our numerical calculations we will assume that the jellium has the same density as bulk sodium, giving a radius of Na₂₀ of $R=5.7$ Å.

Before discussing the coupling of plasmons to cluster vibrations, we first consider the dependence of surface-plasmon frequencies on the shape of the conducting jellium surface. We shall consider only small deviations from a sphere, and shall adopt a parametrization for ellipsoidal shapes where the major axis is the sphere radius elongated by a factor $e^{+2\epsilon}$, and the two minor axes are shrunk by a factor $e^{-\epsilon}$. This scaling transformation thus preserves the volume of the object. To lowest order, the distortion may be described by a quadrupole field with azimuthal symmetry. For this given ellipsoidal shape of the jellium cluster, the plasmon frequency can be obtained from the electrostatic restoring force against rigid displacements of the electrons with respect to the jellium background and the inertia of the electrons. For oscillations along the symmetry axis, the resulting plasma frequency depends on the jellium sphere deformation according to

$$\frac{d\omega_p}{d\epsilon} = -\frac{6}{5}\omega_M, \quad (1)$$

where $\omega_M = (4\pi e^2 n_0 / 3m)^{1/2}$ is the Mie frequency. There are two other plasmon components shifted upward in frequency by $\frac{3}{5}\omega_M\epsilon$. However, in the following discussion we need only consider plasmon oscillations along the

symmetry axis. Deformations with a different azimuthal symmetry with respect to the axis of the plasmon oscillation do not affect its frequency in this order, and we therefore neglect them. A schematic diagram of plasmon excitations in spherical and deformed clusters is given in Fig. 1.

We next discuss the deformation of the jellium sphere. The deformation energy is quite different depending on whether the motion is fast or adiabatic. In the former case, the electronic configuration is frozen, while in the latter case the electrons move to the lowest levels. The schematic energy function in Fig. 1 shows both the diabatic energy surfaces (solid line) and the adiabatic envelope (dotted line). We estimate the energy for the diabatic curve assuming that the electron wave functions change by the same coordinate scaling transformation that defines the ellipsoid. The electronic kinetic energy E_{kin} is affected much more than the potential energy, since the potential is defined by the jellium density which is preserved under the transformation. The kinetic energy can be calculated from

$$E_{\text{kin}}(\epsilon) = N \left[\frac{\langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle}{2m} \right] \\ = E_{\text{kin}}(0) \left[\frac{e^{-2\epsilon} + e^{-2\epsilon} + e^{4\epsilon}}{3} \right]. \quad (2)$$

The spring constant for ellipsoidal deformations is then given by

$$K_d = \left. \frac{d^2 E_{\text{kin}}(\epsilon)}{d\epsilon^2} \right|_0 = 8E_{\text{kin}}(0). \quad (3)$$

Here, the subscript d denotes a diabatic deformation energy function, which we distinguish from an adiabatic function discussed below. Numerical estimates of E_{kin} can be made using the Fermi-gas model or the

harmonic-oscillator model for the electron wave functions. In the Fermi gas model, $E_{\text{kin}}(0) = 3Np_F^2/10m$, where p_F is the Fermi momentum. The corresponding harmonic oscillator estimate gives the result of the Clemenger-Nilsson model.⁷ Numerically, the deduced spring constant for Na_{20} is $K_d = 320$ eV (Fermi gas) and 280 eV (harmonic oscillator).

In the adiabatic case, a jellium cluster is subjected to a strong deformation and the electronic configuration undergoes a major rearrangement. This electronic relaxation can restore the electronic momentum distribution in momentum space to a spherical shape, in which case the electrons' kinetic energy remains nearly the same. Then the surface energy, associated with the surface tension, is the major determinant of the deformation energy. The surface area of an ellipsoid is given by⁸

$$S = 4\pi R^2 \left(1 + \frac{4}{5}\epsilon^2 + \dots \right). \quad (4)$$

Then, the adiabatic spring constant associated with the increase in surface energy is

$$K_a = \gamma 4\pi R^2 \frac{8}{5}, \quad (5)$$

where γ is the surface tension. Of course, K_a is not a true restoring force constant because the electronic configurations are different. Using, as a rough estimate, for small clusters the bulk value of the surface tension of sodium,⁹ $\gamma = 0.20 \text{ J/m}^2$, we find the numerical value of the adiabatic spring constant in Na_{20} , $K_a = 8$ eV.

We next ask what is the appropriate energy surface to calculate the thermal distribution of deformations. The adiabatic surface is appropriate if many states can be populated at a given temperature, i.e., if the energy difference between the ground state and nearby minima is small compared to kT . In that case, the thermal fluctuation will dominate the zero-point motion if the vibrational frequencies calculated from the adiabatic potential are also smaller than kT . We estimate the energy difference between adjacent minima using Eq. (3.2) of Ref. 10, and find that the excitation energy of the next configuration is just of the order of kT at room temperature. Thus, our adiabatic surface may somewhat overestimate thermal effects.

To determine the vibrational frequencies of the cluster deformation modes, we used Rayleigh's vibrational principle¹¹ and estimated the inertia I for quadrupolar vibrations.¹² Numerically, for Na_{20} , $I = 4 \times 10^6 \hbar^2 \text{ eV}^{-1}$. The vibrational frequency of the deformation mode may then be obtained from the harmonic formula $\omega_v = (K_d/I)^{1/2}$. For Na_{20} this yields $\hbar\omega_v = 0.008$ eV. This is considerably smaller than the thermal energy at room temperature, so that if the adiabatic motion is allowed, the clusters formed in molecular beams are likely to have several of these vibrational quanta excited on average.

The coupling of the electronic motion to the vibrations causes the dipole strength for a given initial state to be spread over several vibrations in the final state. This will provide a significant plasmon decay channel provided that there are enough of these states available. With harmonic coupling, the strength function $A(\omega)$ may be calculated exactly in closed form. The result is¹³

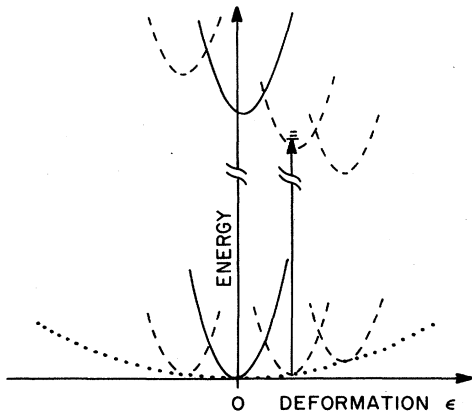


FIG. 1. Schematic diagram of energies of spherical (solid line) and ellipsoidal (dashed line) jellium clusters. The lower line corresponds to the ground-state electron configuration and the upper line is the plasmon excited state. Possible transitions are indicated by arrows. The dotted line is the energy curve for adiabatic deformations.

$$A(\omega) \approx e^{-g(2f+1)} \sum_{n=-\infty}^{+\infty} I_n(2g[f(f+1)]^{1/2}) e^{n\omega_v/2kT} \times \delta(\omega - \omega_M + (g-n)\omega_v). \quad (6)$$

Here, $f = 1/(e^{\omega_v/kT} - 1)$ is the Bose-Einstein factor, $g = (1/2K_d)(1/\omega_v)(d\omega/d\epsilon)^2$ is a dimensionless electron-phonon coupling constant, and I_n are Bessel functions of imaginary argument. At high temperatures the envelope of the strength function is a Gaussian whose full width at half maximum Γ is just what one would expect classically:

$$\begin{aligned} \Gamma &\equiv \sqrt{8 \ln 2} \langle (\omega - \omega_M)^2 \rangle^{1/2} \\ &= \sqrt{8 \ln 2} \frac{d\omega}{d\epsilon} \langle \epsilon^2 \rangle^{1/2} \\ &\approx 2.3 \frac{d\omega}{d\epsilon} \left[\frac{kT}{K_d} \right]^{1/2}. \end{aligned} \quad (7)$$

Numerically, for Na_{20} and at room temperature, Eq. (7) yields $\Gamma = 0.07$ eV. It is clear that this mechanism is not adequate to explain the observed plasmon width¹⁴ of 0.4 eV if the temperature of the Na_{20} clusters which are observed in Ref. 1 is close to room temperature. In this case, only a few vibration quanta could be excited and contribute to the plasmon line broadening since the coupling constant g is only about 2.

The adiabatic deformation energy curve is much softer and could allow for much larger thermal fluctuations. Applying Eq. (7) with the adiabatic deformation constant K_a gives a linewidth $\Gamma = 0.4$ eV for Na_{20} at room temperature, in agreement with the experiment.¹⁴ Values for higher temperatures and larger cluster sizes are plotted in Fig. 2. Note that the numerical results have been obtained without free parameters, although they have been calculated using physical quantities such as surface energy. We feel that the main uncertainty in our model is our estimate of the adiabatic energy surface. Our model can be tested further by measuring the N and T dependence of the linewidth. Since deviations from spherical shape are much smaller in large clusters for a given deformation energy, we expect that the plasmon linewidth should decrease with increasing cluster size N for a given temperature. The functional dependence of Γ should be $N^{-1/3}$ [see Eqs. (5) and (7)]. On the other hand, for a given cluster

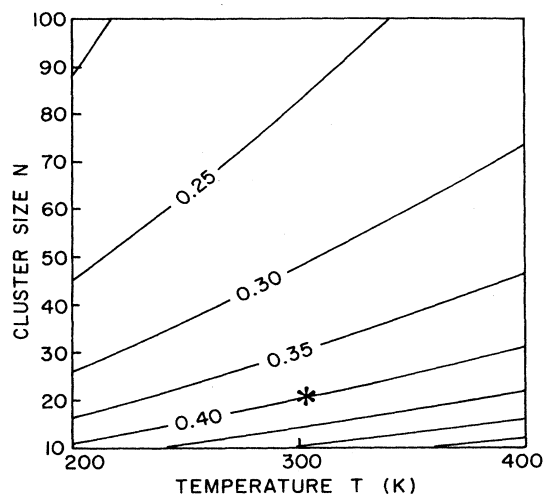


FIG. 2. Contour plot of the plasmon linewidth Γ as a function of the Na cluster size and temperature, as obtained from Eq. (7) and using the adiabatic force constant K_a . The units are eV and the contour interval is 0.05 eV. Room-temperature data for Na_{20} are denoted by *.

size, available deformation energies and hence the linewidth will increase with the square of temperature T [cf. Eq. (7)], as shown in Fig. 2.

In conclusion, it appears that the above described plasmon broadening mechanism is a possible explanation of the plasmon linewidth observed¹ in small clusters such as Na_{20} . This vibrational mechanism also has some definite consequences. First of all, the shape of the plasmon line should be Gaussian rather than Lorentzian. Second, there should be a strong temperature dependence of the line broadening. Third, this mechanism will lose its significance for large cold clusters such as those observed in Ref. 2. At these larger sizes, however, the larger density of electronic states is expected to provide an additional damping mechanism.

The authors acknowledge conversations with W. de Heer, D. Nocera, and W. D. Knight. This research was partly supported by the National Science Foundation under Grant No. PHY-87-14432 and by the Center for Fundamental Materials Research.

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¹⁴Caution is suggested when comparing experimental to theoretical linewidths, since the experimental data were fit with a Lorentzian rather than a Gaussian.