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2003 J. Phys.: Condens. Matter 15 7481

(http://iopscience.iop.org/0953-8984/15/44/004)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 7481–7487 PII: S0953-8984(03)65190-8

Elastic vibrations of spheroidal nanometric particles

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Received 20 June 2003, in final form 26 September 2003
Published 24 October 2003
Online at stacks.iop.org/JPhysCM/15/7481

Abstract

Particles of nanometric size show low-frequency vibrational modes that can be observed by Raman spectroscopy. These modes involve the collective motion of large numbers of atoms and it is possible to calculate their frequency using elasticity theory. In this work a simple model for oblate-shaped nanoparticles is developed and compared with experimental results obtained in bismuth nanoparticles. It is found that the agreement between theory and experiment is improved in comparison to the spherical model usually employed. However for the smallest particles the elastic model is no longer valid and lattice discreteness has to be considered.

1. Introduction

Vibrations of elastic spheres have been studied for a long time by Jaerisch [1], Lamb [2] and Love [3]. More recently this problem has been solved by Torres del Castillo [4] using the spin operators method, which is well suited for decoupling non-scalar equations. However, this author did not take into account any boundary conditions. The spherical case is well understood; normal modes of the sphere can be divided into torsional and spheroidal modes [5]. Tamura *et al* [6] extended the theoretical work by considering different surroundings and thus various boundary conditions for the spheroidal particles. Experimentally such modes have been measured in various situations, from very small structures like globular proteins or inorganic nanoparticles to very large structures like the earth [7, 8]. Surprisingly the Lamb theory is often used to explain the observed results with reasonable agreement [6–8]. For elastic prolate spheroids [5, 9], the equations of torsional modes were first given, unsolved, by Jaerisch [10]. These equations were solved by Rand [11] for the torsional mode in an axisymmetric case.

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Some years ago De Gennes and Papoular [12] suggested that the elastic normal modes of vibrations of globular proteins should be observable by Raman spectroscopy. This technique has revealed itself to be well suited to the study of nanometric-sized systems that show characteristic properties derived from the three-dimensional confinement of electrons and holes as well as of phonons. Such systems have various applications in nonlinear optics, as light emitters in the visible range in the case of silicon nanocrystals (NCs) or as catalytic supports [13]. Raman scattering from confined acoustic phonons has been already reported for some metal and semiconductor NCs [14–17] and proteins [7, 18].

Furthermore this technique was recently used to determine crystallite sizes in the nanometer range in insulators and semiconductors [19–21]. The studied systems consist of NCs embedded in glassy matrix [6], free standing powders [21, 22] or colloidal solutions [23, 24]. The acoustical vibrations appear as low-frequency structured bands which are usually attributed to different types of vibrational modes: breathing, torsional and shearing modes of an elastic sphere. However, one can prove theoretically that shearing and torsional modes are Raman inactive for spherical NCs, but not for spheroidal shaped bodies [25].

Due to the difficulty in controlling the size and shape of nanoparticles, mainly spherical systems have been analysed up to now. It is only recently that other shapes have been obtained and characterized. [14, 26].

In the present work the case of oblate spheroids is analysed and results are compared to experimental Raman scattering measurements on nanometric-size Bi crystals. The Bi NCs were embedded in amorphous germanium thin films and synthesized by pulsed-laser deposition (PLD) [14]. The size and shape have been characterized using various techniques including x-rays and high-resolution transmission electronic microscopy (HRTEM). The mean diameter of the Bi NCs ranged from 2 to 23 nm and their mean height from 0.5 to 6 nm [14].

The Bi NCs are considered as oblate spheroids and the axisymmetric torsional modes are calculated analytically by solving the elastic wave equation in a homogeneous medium in oblate spheroidal coordinates [4, 27]. The effects of a matrix in which the sphere is embedded have been studied by many authors [6, 28, 29]. Usually, different boundary conditions result in a slight shift in the vibrational energy spectra. These authors have also found that new vibration modes may appear, depending on the sphere–matrix coupling. These types of modes are out of the scope of the present work. Thus, the boundary conditions taken into account are a finite solution at the origin and the body surface free of stresses, i.e. we consider no interaction between the particles and the amorphous matrix.

2. Elastic wave equation

The displacement field $\boldsymbol{u}$ obtained in the solution of the equation describing the propagation of an acoustic wave in an elastic medium can be deduced from the scalar and vector displacement potentials, called respectively ϕ and $\boldsymbol{A}$ ($\boldsymbol{u} = \nabla\phi + \nabla \times \boldsymbol{A}$, with $\nabla \cdot \boldsymbol{A} = 0$) [5]. This situation implies a solution to the Helmholtz scalar and vector wave equations for these potentials.

As we know, the Helmholtz vector equation is not separable in spheroidal coordinates, but by considering an axisymmetric potential, i.e.: $\boldsymbol{A} = A_\varphi \hat{\varphi} = A(\xi, \eta)\hat{\varphi}$ [9], where $\hat{\varphi}$ is the unitary vector along the φ coordinate, the vector equation can be derived as

$$\nabla^2 A_\varphi - \frac{A_\varphi}{f^2(1-\eta^2)(\xi^2+1)} + k_{\mathrm{T}}^2 A_\varphi = 0 \tag{1}$$

where ∇^2 is the Laplacian in spheroidal oblate coordinates [29, 30], f is the spheroid focal distance and ξ, η and φ are the spheroidal coordinates, related to the Cartesian coordinates by

$$x = f[(1-\eta^2)(\xi^2+1)]^{\frac{1}{2}} \cos\varphi$$

$$y = f[(1-\eta^2)(\xi^2+1)]^{\frac{1}{2}} \sin\varphi$$
$$z = f\eta\xi$$

with $-1 \leqslant \eta \leqslant 1$, $0 < \xi < \infty$, $0 \leqslant \varphi \leqslant 2\pi$. Here we have chosen the z-axis parallel to the minor axis of the spheroid [30].

Similarly, the scalar displacement potential ϕ will be considered as a function of ξ and η.

In the case of the three-dimensional elastic problem, three components of the displacement, $\boldsymbol{u}_{\mathrm{L}}$, $\boldsymbol{u}_{\mathrm{T1}}$, $\boldsymbol{u}_{\mathrm{T2}}$ are required. They can be expressed like

$$\begin{aligned} \boldsymbol{u}_{\mathrm{L}} &= \nabla\phi = \nabla(R_{ml}(\mathrm{i}h_{\mathrm{L}}, -\mathrm{i}\xi)S_{ml}(\mathrm{i}h_{\mathrm{L}}, \eta)), && m = 0 \\ \boldsymbol{u}_{\mathrm{T1}} &= \nabla \times \boldsymbol{A} = \nabla \times (R_{ml}(\mathrm{i}h_{\mathrm{T}}, -\mathrm{i}\xi)S_{ml}(\mathrm{i}h_{\mathrm{T}}, \eta)\hat{\varphi} && m = 1 \\ \boldsymbol{u}_{\mathrm{T2}} &= \frac{1}{k_{\mathrm{T}}^2}\nabla \times \nabla \times \boldsymbol{A} = R_{ml}(\mathrm{i}h_{\mathrm{T}}, -\mathrm{i}\xi)S_{ml}(\mathrm{i}h_{\mathrm{T}}, \eta)\hat{\varphi} && m = 1 \end{aligned} \tag{2}$$

where h_{L} and h_{T} are defined as the product of the respective longitudinal and transversal wavevector and the focal distance. In these expressions, the spheroidal 'angular' function is given by

$$S_{ml}(\mathrm{i}h, \eta) = \sum_{r=0,1}^{\infty} d_r^{ml}(\mathrm{i}h)P_{m+r}^m(\eta)$$

and the spheroidal 'radial' function R_{ml} is defined as

$$R_{ml}(\mathrm{i}h, -\mathrm{i}\xi) = \frac{(l-m)!}{(l+m)!}\left(\frac{\xi^2+1}{\xi^2}\right)^{m/2} \sum_{r=0,1}^{\infty} \frac{(2m+r)!}{r!}\mathrm{i}^{r+m-l} d_r^{ml}(\mathrm{i}h)\, j_{m+r}(h\xi) \tag{3}$$

where $P_{m+r}^m(\eta)$ are the associated Legendre polynomials and $j_l(h\xi)$ are the spherical Bessel functions. The sum includes even values of r if $(l-m)$ is even or includes odd values of r if $(l-m)$ is odd; for a given m, l is always equal or larger than m. The recursion formula relating successive coefficients d_r^{ml} of equation (3) is

$$\alpha_r d_{r+2}^{ml} + (\beta_r - \lambda_{ml})d_r^{ml} + \gamma_r d_{r-2}^{ml} = 0 \tag{4}$$

where

$$\begin{aligned} \alpha_r &= -\frac{(2m+r+2)(2m+r+1)h^2}{(2m+2r+3)(2m+2r+5)}, \qquad \gamma_r = -\frac{r(r-1)h^2}{(2m+2r-3)(2m+2r-1)}, \\ \beta_r &= (m+r)(m+r+1) - \frac{2(m+r)(m+r+1) - 2m^2 - 1}{(2m+2r-1)(2m+2r+3)}h^2. \end{aligned} \tag{5}$$

The coefficient λ_{ml} is a function of ih; it is the separation constant of equation (1) and at the same time it plays the role of an eigenvalue. In order to obtain the coefficients d_r, we use the matrix method suggested by Aquino *et al* [31] because it permits us to change the matrix size according to the range of h needed to calculate the solutions.

As we can see, the third equation in (2) corresponds to the torsional axisymmetric displacement and looks like the displacement solution given by Rand [11] for the prolate case. The other two equations in (2) can be understood by analogy to the spherical case, as the 'spheroidal modes' of the spheroid, which include the breathing modes.

3. Results and discussion

Considering the boundary conditions, as we said above many authors [2, 6, 15–17] have theoretically studied the vibrational eigenfrequencies of an elastic sphere with a free surface. They show a good agreement between experimental and theoretical results even if these spheres were embedded in a solid matrix. Tamura *et al* [6], and Saviot *et al* [29] have studied the so-called matrix effect as a function of the ratios of the elastic properties of the NCs and the matrix. They have also shown that the remaining eigenvalues suffer slight shifts from those of free vibrations. In a first approximation and according to these results, we shall consider spheroidal particles with free surfaces.

3.1. Torsional vibrations of elastic oblate spheroid

The boundary conditions are specified by the stress tensor $\overleftrightarrow{\sigma}$ [9], or with its projection on the normal vector of the spheroid surface, $\hat{\xi}$. Free vibrations originate when the stresses or forces disappear on the surface at $\xi = X$; then we have

$$\boldsymbol{F}_{\xi=X} = \overleftrightarrow{\sigma} \cdot \hat{\xi}|_{\xi=X} = 0. \tag{6}$$

The determinant obtained by equation (6) gives us the next transcendental equation associated with the $\boldsymbol{u}_{T2}$ component of the displacement, which corresponds to the oblate torsional modes, in analogy with the result given by Rand [11] for prolate shaped bodies:

$$\frac{X^2+1}{X}\frac{\mathrm{d}}{\mathrm{d}X}R_{1l}(\mathrm{i}h_\mathrm{T}, -\mathrm{i}X) - R_{1l}(\mathrm{i}h_\mathrm{T}, -\mathrm{i}X) = 0. \tag{7}$$

Unfortunately, breathing and more complicated modes cannot be obtained because in the determinant (6) the variables cannot be separated. Finally, from equation (7) we can obtain the vibration frequency (in cm^{-1}):

$$\omega_{\mathrm{oblate}} = \frac{C_\mathrm{T}}{2\pi c}\frac{h_{\mathrm{T}n}X}{b}, \tag{8}$$

a and b being the major and minor semi-axis of the spheroids, respectively; $h_{\mathrm{T}n}$ is the nth root of equation (7), and c the velocity of light. The above expression reduces to the spherical torsional formula when the spheroid becomes a sphere [32]. The X-value of the spheroidal surface is easily obtained:

$$X_{\mathrm{oblate}} = \frac{b}{f} = \frac{b}{\sqrt{a^2-b^2}}. \tag{9}$$

By taking the limit $f \to 0$, $X \to \infty$ and $fX \to R$, the sphere radius, equation (7) becomes

$$\frac{\mathrm{d}j_l(\alpha)}{\mathrm{d}\alpha} - \frac{j_l(\alpha)}{\alpha} = 0 \qquad (l \geqslant 1) \tag{10}$$

where $\alpha = k_\mathrm{T}R$.

As one would expect, the above expression is the torsional spherical eigenmode equation.

In our calculation, the formalism of elasticity theory [5, 9] is used, in contrast to Rand's solution [11] in which only symmetry arguments are used to solve elastic wave equation. Unfortunately, as stated above, it has not been possible to obtain other modes than the torsional. In [9], the problem of a degenerate prolate spheroidal cavity ($\xi = 1$) with a harmonic pressure as boundary condition is solved. However, it is solved with approximations and not for all cases; furthermore, the axisymmetric torsional modes related to the $\boldsymbol{u}_{T2}$ displacement component are not treated explicitly.

3.2. Low frequency modes in bismuth nanoparticles

Bi nanoparticles present three Raman active vibration modes in the low-frequency region [14]. The two highest frequency modes present a very small shift with size as they vary from 97.2 to 86.8 cm^{-1} and from 73 to 66.2 cm^{-1} when the size decreases, respectively (figure 1).

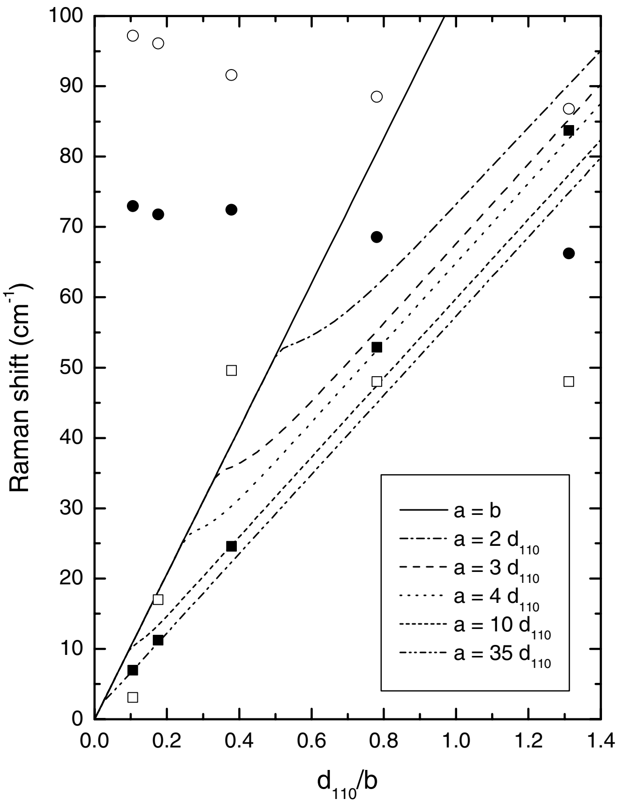

Figure 1. Calculated frequencies of oblate ($b \leqslant a$) spheroids ($m = 1, l = 1$) with increasing semi-axis a and comparison with experimental results. The straight line represents the spherical torsional model. Experimental optical phonons (○, ●) and low-frequency modes (□) are from [14]. (■) are the calculated frequencies for parameters corresponding to the same samples of [14].

The lowest frequency mode has very different behaviour, as its frequency varies from 3 to 48 cm^{-1} as the b semi-axis varies from 3.09 to 0.25 nm. These results show unambiguously that the lowest frequency mode is strongly size dependent and is not an ordinary Raman mode. Moreover, the same authors have performed polarized Raman scattering and have shown that this mode is not polarized. The same spectral shape is obtained in parallel and crossed polarizations. This justifies our choice to compare them with calculated torsional modes rather than breathing modes.

The axisymmetric solution of the sphere corresponds to the eigenvalue $m = 0$, but in the spheroidal case, the axisymmetric torsional modes are given for $m = 1$, and for the l-values with the condition given above. In figure 2, the torsional mode ($l = 1, m = 0$) [5] for a sphere is represented schematically. However, this kind of movement is the limit of the torsional case of a spheroidal shape body. In this last case, the vibration mode also contains a linear combination of products of a Bessel function and an associated Legendre polynomial of superior orders ($l = 1, 3, \ldots, 2n + 1, \ldots, \infty$). Such a linear combination also transforms into only one product when we go to the spherical limit.

The different parameters for the five Bi NCs studied are given in table 1. Figure 1 shows the eigenfrequencies calculated for $l = 1$ and $m = 1$ together with experimental measurements from low-frequency Raman experiments; the x-axis is given in terms of the inverse of the minor

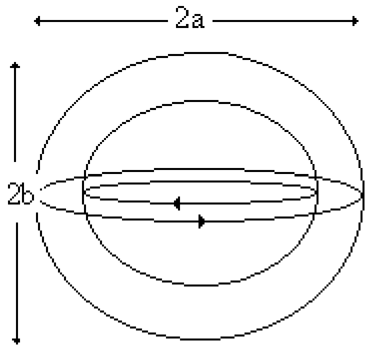

Figure 2. A representation of the $l = 1$, $m = 0$, 1 torsional mode for a sphere.

Table 1. Semi-axis values, surface $\xi = X$ value, calculated and experimental frequencies of bismuth nanoparticles.

Sample	BG12	BG25	BG50	BG100	BG200
a (nm)	1.15	1.25	3.5	8.5	11.5
b (nm)	0.25	0.42	0.865	1.865	3.09
X	0.222 718	0.356 740	0.255 055	0.224 892	0.278 954
ω_1 (cm^{-1})	83.7	52.9	24.6	11.2	7.0
ω_{exp} (cm^{-1})	48	48	49.6	17	3

semi-axis b and the lattice parameter d_{110} of Bi of the rhombohedral structure, corresponding to the (012) axis of hexagonal equivalent structure, which is equal to 0.328 nm [14]. The theoretical curves are given maintaining a constant and b varying up to the spherical limit ($b = a$), which gives a straight line also represented in figure 1. The a- and b-values are given as multiples of d_{110}.

We have calculated the frequencies with a- and b-values having the same order of magnitude as the NCs without free parameters. The torsional spherical model is in reasonable agreement for large NCs but fails in the case of the small ones. It has to be mentioned here that the BG25 and BG12 samples have only a few (8) atomic planes. Therefore for the smallest particles the elastic model is no longer valid and lattice discreteness has to be considered. Finally we can observe that the parameter X in table 1, given by (9), is approximately the same for almost all NCs (except BG25); this gives us information about their regular growth, i.e.: we have quasi-homothetic oblate spheroids, and about the benefits of the technique used, in this case the PLD method.

4. Conclusion

In this work, an elastic model is used to analyse the experimental Raman frequencies of acoustic modes of Bi NCs. This model considers a different geometry from the spherical: oblate-shaped nanoparticles. As we have shown, a small change of the sphericity of the particle lowers the frequency vibration according to what is experimentally observed. This elastic model fails to give account for the frequencies of the smallest NCs; in this case a discontinuous treatment of the problem has to be considered.

Acknowledgments

The present work has been partially supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT) of México and the Centre National de la Recherche Scientifique (CNRS) of France through the agreement CONACYT—CNRS for travel support. Thanks are due to Drs E Piña and E Castaño of the UAM-Iztapalapa for helpful and stimulating discussions.

References

[1] Jaerisch P 1880 *J. F. Math. (Crelle)* **88** 131
[2] Lamb H 1882 *Proc. Math. Soc. Lond.* **13** 187
[3] Love A E H 1944 *A Treatise on Mathematical Theory of Elasticity* (New York: Dover)
[4] Torres del Castillo G F 1999 *Rev. Mex. Fis.* **45** 557
[5] Morse R M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw-Hill)
[6] Tamura A, Higeta K and Ichinokawa T 1982 *J. Phys. C: Solid State Phys.* **15** 4975
[7] Picquart M, Haro-Poniatowski E, Morhange J F, Jouanne M and Kanehisa M 2000 *Biopolymers* **53** 342
[8] Tanimoto T, Um J, Nishida K and Kobayashi N 1998 *Geophys. Res. Lett.* **25** 1553
[9] Eringen A C and Suhubi E S 1975 *Elastodynamics, Linear Theory* vol 2 (New York: Academic)
[10] Jaerisch P 1889 *J. F. Math. (Crelle)* **104** 177
[11] Rand R H 1968 *J. Acoust. Soc. Am.* **44** 749
[12] de Gennes P G and Papoular M 1969 *Polarisation, Matière et Rayonnement, Volume in Honor of Alfred Kastler* (Paris: Presses Universitaires de France) p 243
[13] Mercera P D L, Van Ommen J G, Doesburg E B M, Burgraaf A J and Ross J R H 1990 *Appl. Catal.* **57** 127
[14] Haro-Poniatowski E, Jouanne M, Morhange J F, Kanehisa M, Serna R and Afonso C N 1999 *Phys. Rev.* B **60** 10080
[15] Fujii M, Nagareda T, Hayashi S and Yamamoto K 1991 *Phys. Rev.* B **44** 6243
Fujii M, Nagareda T, Hayashi S and Yamamoto K 1995 *Phys. Rev.* B **52** 14273 (erratum)
[16] Fujii M, Kanzawa W, Hayashi S and Yamamoto K 1996 *Phys. Rev.* B **54** R8373
[17] Champagnon B, Adrianasolo B, Ramos A, Gandais M, Allais M and Benoit J P 1993 *J. Appl. Phys.* **73** 2775
[18] Painter P C and Mosher L E 1982 *Biopolymers* **18** 3121
[19] Champagnon B, Andrianasolo B and Duval E 1991 *Mater. Sci. Eng.* B **9** 417
[20] Duval E, Boukenter A and Champagnon B 1986 *Phys. Rev. Lett.* **56** 2052
[21] Jouanne M, Morhange J F, Kanehisa M, Haro-Poniatowski E, Fuentes G A, Torres E and Hernández Tellez E 2001 *Phys. Rev.* B **64** 155404
[22] Gotic M, Ivanda M, Popovic S, Music S, Sekulié A, Turkovic A and Furic K 1997 *J. Raman Spectrosc.* **28** 555
[23] Verma P, Cordts W, Irmer G and Monecke J 1999 *Phys. Rev.* B **60** 5778
[24] Genzel L, Keilmann F, Martin T P, Winterling G, Yacoby Y, Fröhlich H and Makinen M W 1976 *Biopolymers* **15** 219
[25] Duval E 1992 *Phys. Rev.* B **46** 5795
[26] Kofman R, Cheyssac P, Aouaj A, Lereah Y, Deutscher G, Ben-David T, Penisson J M and Bourret A 1994 *Surf. Sci.* **303** 231
[27] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)
[28] Ovsyuk N N and Novikov V N 1996 *Phys. Rev.* B **53** 3113
[29] Saviot L, Murray D B and del Carmen de Lucas M 2003 *Preprint* cond-mat/0307634 v1
[30] Hanish S, Baier R V, Van Buren A L and King B J 1970 *Tables of Radial Spheroidal Waves Functions* vol 4 (Washington, DC: Naval Research Laboratory, Transducer Branch, Acoustics Division)
[31] Aquino N, Castaño E and Ley-Koo E 2002 *Rev. Mex. Fis.* **48** 277
[32] Stratton J A, Morse P M, Chu L J, Little D C and Corbató F J 1956 *Spheroidal Wave Functions* (New York: Wiley)