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# Phonon spectrum in a nanoparticle mechanically coupled to a substrate

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## Abstract

We calculate the vibrational density-of-states in an insulating nanoparticle that is in weak mechanical contact with a semi-infinite substrate. The work is motivated by a recent experiment by Yang et al., where the low-energy phonon density-of-states of  $Y_2O_3$  nanoparticles doped with  $Eu^{3+}$  was measured. Preliminary results presented here, based on the conventional quasiparticle-pole approximation for the phonon propagator, are in reasonable agreement with experiment. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

As is well known, the vibrational spectrum of an isolated nanometer-scale crystal is discrete. For a spherical nanoparticle of diameter  $d$  and bulk transverse sound velocity  $v_t$ , the lowest internal vibrational mode, called the Lamb mode, has a frequency of about  $2\pi v_t/d$ . Below this frequency, no internal vibrational modes exist, and the phonon density-of-states (DOS) vanishes. Any property of the nanoparticle that depends on this vibrational spectrum, such as its thermodynamic properties or electron–phonon dynamics, will therefore be very different, especially at low energies, when compared to bulk crystals made of the same material.

In an interesting recent experiment, Yang et al. [1] measured the DOS of  $Y_2O_3$  nanoparticles with a size distribution ranging from 7 to 23 nm in diameter. Nanoparticles of size, say, 15 nm, cannot support phonons with energies below about  $10\text{ cm}^{-1}$ . The phonon DOS was obtained by measuring the nonradiative lifetime of an excited electronic state of  $Eu^{3+}$ , and at  $3\text{ cm}^{-1}$  was found to be about 100 times smaller than that of a bulk  $Y_2O_3$  crystal.

In this paper we propose and investigate a mechanism to explain the observed low-energy DOS. Several phonon-broadening mechanisms could be responsible for this effect. For example, anharmonicity causes the modes to broaden, leading to a DOS at low energy. However, anharmonicity is ineffective at low energy and an estimate of the anharmonic broadening showed that the resulting DOS is much smaller than that observed [2]. Adsorbed molecules or “dirt” on the

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outside of the nanoparticle could also be involved. A more likely broadening mechanism results from the fact that these nanoparticles are not isolated, but rather are in contact with each other or some support structure. This contact enables the nanoparticles to couple to an environment with a continuous vibrational spectrum at low energy. We believe that it is this mechanical coupling to the environment that broadens the vibrational modes enough to explain the observed DOS.

Our preliminary results, presented here, are favorable. However, the calculation has only been done within the conventional quasiparticle-pole approximation for the nanoparticle phonon propagator [3], which, to leading order in perturbation theory, is equivalent to using Fermi's golden rule to obtain vibrational-mode lifetimes and assuming Lorentzian line shapes. A more accurate calculation of the nanoparticle DOS, which requires the solution of the Dyson equation, will be presented in future work.

## 2. Model and method

Our model consists of a single isotropic elastic sphere of diameter 10 nm, representing the nanoparticle, connected to a semi-infinite isotropic elastic continuum lying in the  $xy$  plane and extending to infinity in the negative  $z$  direction. For simplicity, we take the substrate and the nanoparticle to be made of the same material. We model the contact between the two by a weak harmonic spring, corresponding to the situation where the nanoparticle and substrate are connected by only a few atomic bonds or by a small "neck" of material. The Hamiltonian for the system is

$$H = \sum_J \hbar\omega_J a_J^\dagger a_J + \sum_I \hbar\omega_I b_I^\dagger b_I + \frac{1}{2} K [u_z(\mathbf{r}_0)_{\text{part}} - u_z(\mathbf{r}_0)_{\text{sub}}]^2, \quad (1)$$

where the  $a_J$  and  $a_J^\dagger$  are annihilation and creation operators for phonons in the nanoparticle, and the index  $J$  runs over all the modes of the nanoparticle.

The  $b_I$ ,  $b_I^\dagger$ , and  $I$  correspond to the substrate phonons.<sup>1</sup> The spring constant  $K$  is taken to be of the order of an atomic bond strength of the material.  $u_z(\mathbf{r}_0)_{\text{part}}$  and  $u_z(\mathbf{r}_0)_{\text{sub}}$  are the  $z$  components of the phonon displacement field of the nanoparticle and the substrate respectively, evaluated at the point of connection  $\mathbf{r}_0$ .

The displacement field for the nanoparticle can be expanded as

$$\mathbf{u}(\mathbf{r}, t)_{\text{part}} = \sum_J \sqrt{\frac{\hbar}{2\rho\omega_J}} [a_J \Psi_J(\mathbf{r}) e^{-i\omega_J t} + \text{H.c.}], \quad (2)$$

where the  $\Psi_J(\mathbf{r})$  are the nanoparticle vibrational eigenmodes, normalized according to

$$\int_V d^3r \Psi_J^*(\mathbf{r}) \cdot \Psi_{J'}(\mathbf{r}) = \delta_{JJ'}, \quad (3)$$

where  $\rho$  is the mass density.  $V$  is the volume of the nanoparticle. The nanoparticle's vibrational eigenmodes were found by using a method similar to the one used by Lamb [4].

Similarly, the substrate displacement field is given by

$$\mathbf{u}(\mathbf{r}, t)_{\text{sub}} = \sum_I \sqrt{\frac{\hbar}{2\rho\omega_I}} [b_I \mathbf{f}_I(\mathbf{r}) e^{-i\omega_I t} + \text{H.c.}], \quad (4)$$

with the  $\mathbf{f}_I$  normalized as above. The vibrational eigenmodes of the substrate were calculated following Ezawa [5].

To determine the vibrational DOS we calculate the retarded Green's function for the nanoparticle,  $D^{ij}(\mathbf{r}, \mathbf{r}', t) \equiv -i\theta(t) \langle [u^i(\mathbf{r}, t), u^j(\mathbf{r}', 0)] \rangle$ .

Evaluating this perturbatively to second order in the spring constant  $K$ , and using the quasiparticle-pole approximation [3] (which replaces the energy-dependent phonon self-energy for each mode  $J$  with its on-shell value), we find the energy damping rate for mode  $J$  to be given by

$$\tau_J^{-1} = \frac{\pi K^2}{\hbar\rho} \frac{N_s(\omega_J)}{\omega_J} |\Psi_{J^z}(\mathbf{r}_0)|^2, \quad (6)$$

where

$$N_s(\omega) \equiv -\frac{1}{\pi} \text{Im} D_s^{zz}(\mathbf{r}_0, \mathbf{r}_0, \omega) \quad (7)$$

<sup>1</sup> Because the substrate is semi-infinite, the label  $I$  assumes both discrete and continuous values.

is the phonon spectral density at the surface of the substrate and  $D_s^{ij}(\mathbf{r}, \mathbf{r}', \omega)$  is the transform of the substrate propagator. Eq. (6) can also be derived from Fermi's golden rule. The quasiparticle-pole approximation predicts Lorentzian-broadened line shapes. This leads to a nanoparticle DOS given by

$$g(\varepsilon) = \sum_J \frac{\hbar\tau_J^{-1}/\pi}{(\varepsilon - \hbar\omega_J)^2 + \hbar^2\tau_J^{-2}} \quad (8)$$

The usual thermodynamic DOS (number of states per unit energy per unit volume) is given by  $g(\varepsilon)/V$ , where  $V$  is again the volume of the nanoparticle.

### 3. Results and conclusions

For simplicity, we assume the nanoparticle and substrate to be made of Si, thus enabling us to obtain the surface spectral density (7) from Appendix B of Ref. [6]. We treat Si as an isotropic

elastic continuum with longitudinal and transverse sound velocities

$$v_l = 8.5 \times 10^5 \text{ cm s}^{-1},$$

$$v_t = 5.9 \times 10^5 \text{ cm s}^{-1}, \quad (9)$$

and mass density  $\rho = 2.3 \text{ g cm}^{-3}$ . For a spring stiffness  $K = 1.0 \times 10^4 \text{ erg cm}^{-2}$ , we obtain the phonon DOS shown in Fig. 1.

Our calculation includes all modes below a cutoff frequency  $\omega_{\max}$  of  $100 \text{ cm}^{-1}$ . The low-energy DOS depends, to some extent, on our choice of  $\omega_{\max}$ . This sensitivity is an artifact of the quasiparticle-pole approximation, or equivalently, a consequence of assuming Lorentzian line shapes. Because at this stage we are only interested in whether our result agrees with the experiment of Ref. [1] at the order-of-magnitude level, we will not discuss the weak  $\omega_{\max}$  dependence any further.

Fig. 2 shows the low-energy DOS up to about  $15 \text{ cm}^{-1}$ . The large peak on the right is the

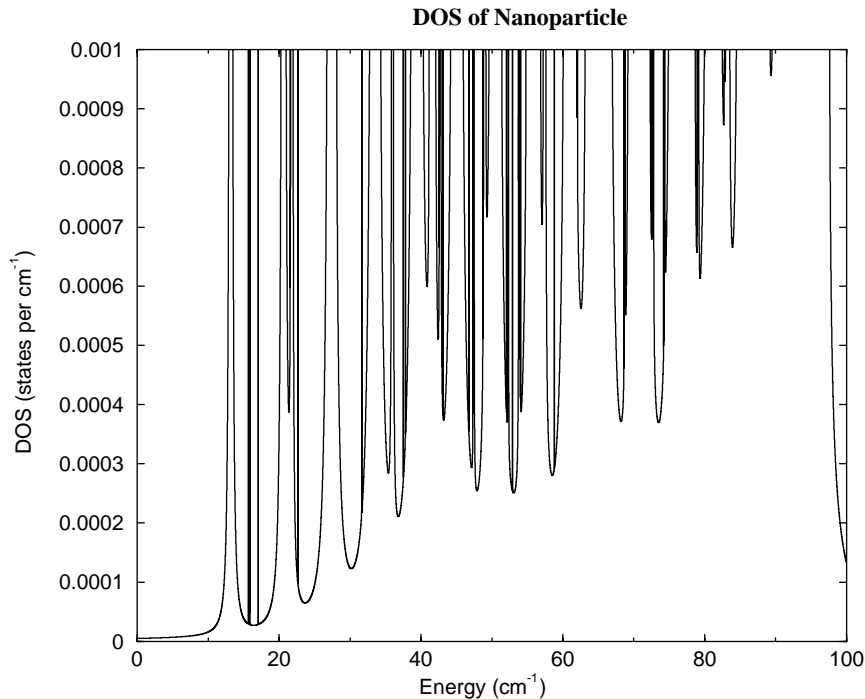


Fig. 1. Vibrational DOS in a 10 nm Si nanoparticle, weakly coupled to a substrate. The DOS rapidly approaches the bulk Debye law.

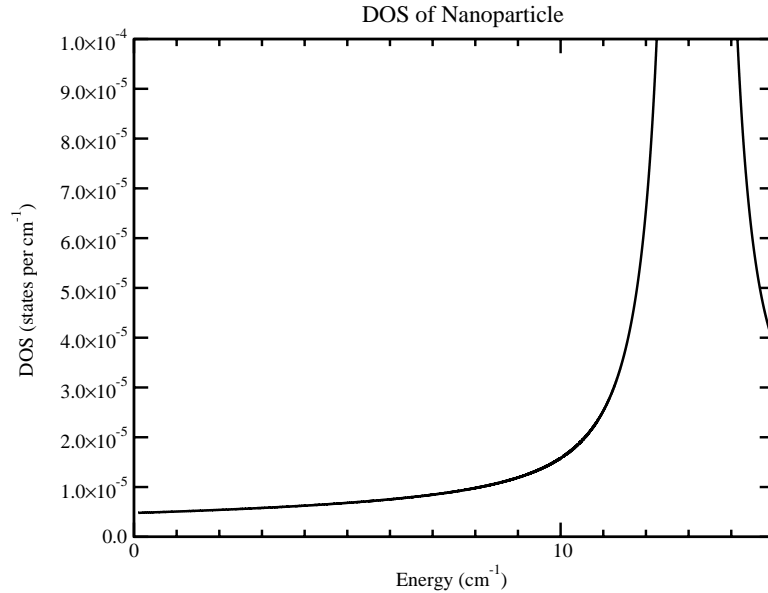


Fig. 2. Low-energy DOS.

five-fold-degenerate Lamb mode. At  $3 \text{ cm}^{-1}$ , the DOS is found to be  $5.8 \times 10^{-6} \text{ states cm}^{-1}$ ,<sup>2</sup> or about  $3.2 \times 10^{-4}$  times the bulk DOS<sup>3</sup>

$$\sum_{\lambda} \frac{\varepsilon^2}{2\pi^2 \hbar^3 v_{\lambda}^3} \cdot V = 2.0 \times 10^{-3} E^2 \text{ states cm}^{-1}, \quad (10)$$

where  $E$  is the energy in  $\text{cm}^{-1}$ . Experimentally, the ratio of nanoparticle to bulk DOS was found to be approximately  $7.4 \times 10^{-3}$ , about 20 times larger than our result.

This is a good result considering the simplicity of our model. However, the quasiparticle-pole approximation is probably inaccurate much below  $10 \text{ cm}^{-1}$ , where the deviation from Lorentzian line shapes becomes important. However, the order-of-magnitude agreement does suggest that we have correctly identified the relevant broadening mechanism in these nanoparticles. An accurate calculation of the nanoparticle DOS, based on the solution of the Dyson equation, is in progress.

<sup>2</sup>Reducing  $\omega_{\text{max}}$  to  $80 \text{ cm}^{-1}$  lowers the DOS at  $3 \text{ cm}^{-1}$  to about  $4.9 \times 10^{-6} \text{ states cm}^{-1}$ .

<sup>3</sup>The standard Debye formula has to be multiplied by  $V$  to make comparison to Eq. (8) possible.

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