Phonons in an Inhomogeneous Continuum: Vibrations of an Embedded Nanoparticle

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The spectrum of acoustic vibrational modes of an inhomogeneous elastic continuum are analyzed with application to a spherical nanoparticle embedded in an infinite glass block. The relationship of these modes to the discrete vibrational spectrum of a free sphere is studied. The vibrational modes of a sphere with a fixed surface are relevant in some situations. Comparisons are also made to calculations of mode frequency and damping based on complex valued frequency.

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I. INTRODUCTION

In 1882, Lamb\textsuperscript{1} calculated the frequencies of vibration of a free isotropic homogeneous continuous sphere. Twenty years ago\textsuperscript{2,4} this model was applied to nearly spherical atomic clusters a few nanometers in size (nanoparticles), whose vibrations can be observed by low frequency inelastic light scattering (Raman or Brillouin setups depending on the actual particle size) and also by femtosecond pump-probe experiments.\textsuperscript{5} However, with exceptions\textsuperscript{5,6,7,8,9,10} the free sphere model hardly seems applicable because the samples investigated are doped glasses, \textit{i.e.} nanoparticles solidly embedded within a glass matrix.

Variations on Lamb’s calculation attempt to take into account the mechanical properties of the matrix. The nanoparticle surface can be rigidly fixed.\textsuperscript{11,12,13} Assuming outgoing travelling waves in the matrix, complex valued mode frequencies can be found.\textsuperscript{12,13} These approaches give discrete sets of vibrational modes, unlike a macroscopic object in which there is a continuum.

Conversely, the nanoparticle-matrix interface influence on vibrations can be ignored\textsuperscript{14} and bulk phonon modes can be used as if the nanoparticle surface were acoustically invisible. This latter approach can be workable when other mechanisms, such as size quantization of nanoparticle electron energy levels (excitons), provide the dominant contribution to the qualitative features of light scattering spectra.

None of the foregoing provides a satisfactory description of a nanoparticle-matrix system even if they can provide valuable insight. What is needed is a calculation that properly models the effect of the presence of the nanoparticle on the phonon modes. In this paper, we present such an approach based on recent calculations on core-shell systems.\textsuperscript{15}

Apart from some general observations made in section II, the nanoparticle is idealized as an isolated spherical homogeneous isotropic classical continuum object embedded in similarly idealized glass. Departures from this won’t be addressed in this paper even though they can be experimentally important. Taking into account nanoparticle size distribution is straightforward. Anisotropy has been discussed in a previous paper\textsuperscript{13} and here we use directionally averaged sound speeds calculated as described therein. Non-sphericity is a more complex problem but arbitrary shapes can be investigated using molecular dynamics simulation.\textsuperscript{15} Application of continuum elastic boundary conditions at the interface between nanoparticle and matrix is also an idealization that needs to be justified with attention to details at the microscopic level. For example, such conditions are generally incorrect for epitaxial interfaces.\textsuperscript{15}

Mode frequencies predicted for a free sphere correspond to dampened motions at the same frequency of the nanoparticle in a sufficiently soft and light matrix. Some qualitatively new modes appear corresponding to semi-rigid libration (angular oscillation) and rattling (translational oscillation) of the nanoparticle as a result of the elastic restoring force provided by the matrix. Mode frequencies for a sphere with a fixed boundary correspond to the dampened motions of a nanoparticle in a harder and denser matrix.

II. GENERAL INHOMOGENEOUS SYSTEM

Although subsequent sections of the paper deal with isotropic and homogeneous materials, it is useful to first consider a continuous elastic medium which may be inhomogeneous and anisotropic. \( \mathbf{r}(\mathbf{R}, t) \) denotes real space coordinates of the point of matter which has material coordinate \( \mathbf{R} \). Deviation from equilibrium is described in terms of the displacement field \( \mathbf{u}(\mathbf{R}, t) = \mathbf{r}(\mathbf{R}, t) - \mathbf{R} \). The mass density of the medium is \( \rho(\mathbf{R}) \). Note that this density refers to material coordinates. The density in real space coordinates varies as acoustic vibrations in the medium cause local expansion and contraction.

The elastic constants of the material are \( c_{ijkl}(\mathbf{R}) \). Stress \( \sigma_{ij} \) is related to the displacement field through \( \sigma_{ij} = c_{ijkl}\mathbf{u}_{kl} \) where a summation is implied over repeated indices and the comma implies a partial deriva-
The equation of motion is $\rho(\vec{R})\ddot{\vec{u}}_i = \sigma_{ij,j}$.

Six different models, with abbreviations listed in Table III, have been studied. For some of them (BSM, FSM and CSM) $\vec{u}$ is real valued. For the others, $\vec{u}$ is complex valued, but the imaginary part of $\vec{u}$ is to be ignored.

The equation of motion has normal modes $\vec{u}_n(\vec{R})$ with frequency $\omega_n$, where $n$ is a mode index. The angular frequency $\omega$ (in rad/s) is related to the wavenumber $\nu$ (in cm$^{-1}$) through $\nu = \omega/(200\pi c)$ where $c$ is the speed of light (in m/s). Modes are orthonormalized using

$$\int \rho(\vec{R})\vec{u}_i(\vec{R}) \cdot \vec{u}_j(\vec{R}) d^3\vec{R} = \delta_{ij} M_{p+m}$$

for any two modes $i$ and $j$, where $M_{p+m}$ is the mass of the system (nanoparticle and matrix). The integration is over the volume of the system. Equation (1) is justified in Appendix A. A general disturbance of the system has displacement field

$$\vec{u}(\vec{R}, t) = \sum_n \left(x_n \sin(\omega_n t) + y_n \cos(\omega_n t)\right) \vec{u}_n(\vec{R})$$

On the basis of the normalization chosen, $\vec{u}_n(\vec{R})$ is dimensionless. Therefore $x_n$ and $y_n$ have units of metres.

Inserting (2) into (A1) and (A2) and simplifying using (A6) and (A7), the total energy of the system is

$$E = \frac{1}{2} M_{p+m} \sum_n \omega_n^2 (x_n^2 + y_n^2)$$

### III. SPHERICALLY SYMMETRIC MODELS

In this and later sections the displacement field depends on spherical material coordinates $\vec{R} = (R, \theta, \phi)$. The nanoparticle ($"p"$) is idealized as a homogeneous and isotropic sphere of radius $R_p$ and density $\rho_p$ with speeds of sound $v_p^L$ and $v_p^T$.

In the free sphere model (FSM), the nanoparticle surface at $R = R_p$ is free. Mode frequencies are $\omega^{FSM}_{lmnq}$ where $q$ can be spheroidal (SPH) or torsional (TOR), $l$ and $m$ are angular momentum and its $z$-component, and $n$ is the harmonic index. For convenience, these modes will be called "pseudomodes" when referring to situations of a sphere that is only weakly coupled to its surroundings. Several incorrect calculations of the FSM (SPH,$l=0$) modes appear in the literature.

In the bound sphere model (BSM), the nanoparticle surface is rigidly fixed. Mode frequencies are $\omega^{BSM}_{lmnq}$.

In the complex frequency model (CFM), the nanoparticle is surrounded by a homogeneous and isotropic matrix ($"m"$) of density $\rho_m$ and speeds of sound $v_m^L$ and $v_m^T$. The matrix extends to infinity. Continuity of $\vec{u}$ and force-balance apply at the nanoparticle-matrix interface. The boundary condition at large $R$ is that $\vec{u}$ is an outgoing travelling wave. The mode frequencies $\omega^{CFM}_{lmnq}$ are complex valued. In spectroscopic observations of such a mode (a plot of scattered light intensity versus wavenumber $\nu$) a broadened peak is observed with its center at $\nu = \text{Re}(\omega)/(200\pi c)$ and with a half width at half maximum (HWHM) of $\text{Im}(\omega)/(200\pi c)$.

Other workers used the "absolute value of the spherical Hankel function" for the outgoing wave, artificially reducing the mathematical problem to real-valued frequencies.

There are two important limiting cases of CFM: In the rigid complex frequency method (RCFM) the nanoparticle is made infinitely rigid and heavy. In the void complex frequency method (VCFM) the nanoparticle is replaced by an empty void.

CFM, RCFM and VCFM necessarily have complex-valued $\vec{u}$ which blows up exponentially with $R$ and cannot be orthonormalized. Equations (1) to (4) and the discussion in Appendix A are for FSM, BSM and CSM only and do not apply to CFM, RCFM and VCFM.

### IV. CORE-SHELL MODEL

Adapting the core-shell model (CSM) we consider a nanoparticle as in the previous section concentrically within a much larger homogeneous and isotropic sphere (representing the glass matrix) with radius $R_m$. In the macroscopic limit $R_m$ goes to infinity, and the frequency of every vibrational mode varies as $1/R_m$ and therefore goes to zero. Going from the FSM to an embedded sphere with a macroscopic matrix means changing from a discrete set of vibrational modes to a continuum.

We are primarily interested in Raman or Brillouin experiments in which light is scattered from the nanoparticle rather than from the transparent matrix material. Low frequency vibrations of the nanoparticle allow the scattered photon to have wavenumber a few cm$^{-1}$ above or below those in the incident laser beam. The general idea behind this core-shell approach is that although the vibrations of the whole system are described by a continuum of modes, the nanoparticle doesn’t move as much for matrix phonons of certain wavelengths.

The inelastically scattered light is modulated by the frequency-dependent amplitude of the vibration within
the nanoparticle. The mechanism for the photon scattering process depends on the electronic details of the nanoparticle: In semiconductors, bound excitons; In metals, resonant plasmons; In insulators, strain-optic coupling. In any case, a preliminary step is to study the amplitude of nanoparticle vibrations as a function of phonon frequency. That is the goal of our present investigation.

The first step is to solve the equation of motion for a given value of \( R_m \). Extending Takagahara’s work to core-shell systems, the normal modes have displacement fields \( \vec{u}_{lmnq} \) which are normalized with respect to Eq. (1).

Orthogonality of the modes was also checked numerically.

For the results reported here, the outer surface of the matrix has zero traction force boundary conditions. However, we have verified that use of zero displacement boundary conditions has no noticeable consequence on the figures presented in this paper. Eigenfrequencies are affected, but because we are interested in the macroscopic limit \( (R_m/R_p \to \infty) \) this is not important.

To connect CSM with the FSM, BSM and CFM models, we compare the discrete frequency sets to the position and width of peaks of the mean square displacement inside the nanoparticle (Eq. (4) where \( \vec{u}_{lmnq} \) is obtained from CSM) as a function of frequency.

\[
\langle u_{lmnq}^2 \rangle_p = \frac{1}{3\pi R_p^2} \int_{R<R_p} \langle \vec{u}_{lmnq}(\vec{R}) \rangle^2 d^3\vec{R} \tag{4}
\]

Using the selection rules predicted by Duval, one can get a rough idea of what the reduced Raman spectrum might look like: only (SPH, \( l=0 \)) and (SPH, \( l=2 \)) modes are Raman active for a spherical isotropic nanoparticle under non-resonant excitation.

The mean square displacement \( \langle u^2 \rangle_p \) that we plot in our figures is only one of many possible measures of the internal motion of the nanoparticle. If we are interested in low-frequency inelastic light scattering, then ultimately we want to calculate the scattered photon spectrum. Our model provides a key ingredient for such a calculation in the \( \vec{u}_{lmnq}(\vec{R}) \). Just as in plane wave vibrational modes, second quantization can be applied to these modes to obtain phonon creation and annihilation operators, which would be required in any model of photon scattering.

The \( \langle u^2 \rangle_p \) variation with the mode frequency is not affected once \( R_m/R_p \) exceeds several times unity. Increasing this ratio results in more vibrational modes for a given frequency range. This increase is compensated by the lower amplitude associated with each mode. In this paper, we use \( R_m/R_p = 100 \) when possible to have continuous looking plots. Calculations with bigger ratios were performed but don’t change the results. Note that \( R_m/R_p = 100 \) means that the nanoparticle occupies 1/1000000 of the total volume.

| \( q \) | \( l \) | \( n \) | FSM \( \nu \) | CFM \( \nu \) | RCFM \( \nu \) |
|-------|-----|-----|-----|-----|-----|
| TOR 2 | 0   | 2   | 2.6 | 5.8 | 2.4 | 4.2 |
|       | 1   | 4.7 | 7.2 | 1.0 |
|       | 2   | 13.5| 13.9| 1.1 |
|       | 3   | 19.8| 20.1| 1.1 |
|       | 4   | 26.0| 26.2| 1.1 |
| TOR 1 | 0   | 2   | 0.0 | 4.5 | 0.0 | 2.8 |
|       | 1   | 4.9 | 1.1 |
|       | 2   | 10.9| 11.4| 1.1 |
|       | 3   | 17.1| 17.5| 1.1 |
|       | 4   | 23.2| 23.5| 1.1 |
|       | 5   | 29.2| 29.4| 1.1 |
| SPH 2 | 0   | 2   | 0.0 | 4.5 | 0.0 | 2.9 |
|       | 1   | 0.0 | 12.0| 10.4|
|       | 2   | 5.0 | 5.8 | 1.4 |
|       | 3   | 8.8 | 9.2 | 8.2 | 7.5 |
|       | 4   | 9.7 | 11.1| 1.2 |
|       | 5   | 16.4| 17.0| 1.1 |
|       | 6   | 21.9| 22.4| 1.6 |
|       | 7   | 23.6| 23.5| 1.5 |
|       | 8   | 29.0| 29.2| 1.1 |
| SPH 1 | 0   | 2   | 2.9 | 1.3 |
|       | 1   | 4.5 | 8.0 | 4.1 | 6.4 |
|       | 2   | 6.9 | 8.4 | 1.2 |
|       | 3   | 13.8| 14.3| 1.1 |
|       | 4   | 17.3| 17.6| 1.9 |
|       | 5   | 20.3| 20.5| 1.2 |
|       | 6   | 26.2| 26.4| 1.1 |
| SPH 0 | 0   | 2   | 0.0 | 6.3 | 0.0 | 5.0 |
|       | 1   | 11.4| 11.9| 1.9 |
|       | 2   | 24.9| 25.1| 1.9 |

TABLE II: Wavenumber (\( \nu \)) and HWHM damping (\( \Delta \nu \)) in cm\(^{-1} \) for free (FSM), BaO-P\(_2\)O\(_5\) embedded Ag nanoparticles (CFM) and rigid nanoparticle (RCFM) for modes with \( \nu < 30 \) cm\(^{-1} \) and \( R_p = 4.9 \) nm.

V. DISCUSSION

A. Ag in BaO-P\(_2\)O\(_5\) glass

Low-frequency inelastic light scattering and femtosecond pump-probe experiments on nearly spherical Ag nanoparticles grown in a BaO-P\(_2\)O\(_5\) (high density glass) matrix show very well resolved features, making it a perfect system to start with.

Elastic parameters for silver at 300K are directionally averaged giving sound speeds 1740 m/s and 3750 m/s. The actual transverse speed of sound in Ag varies from 1195 m/s to 2080 m/s depending on the direction. Longitudinal speed of sound varies from 3410 to 3935 m/s. Rms averaged speeds (1760 m/s, 3750 m/s) are comparable to the average speeds. FSM vibrational frequencies calculated using directionally averaged speeds are in good agreement with frequencies calculated with a molecular dynamic approach which fully takes into account elastic anisotropy. Mass density and sound speeds for the BaO-P\(_2\)O\(_5\) matrix are taken from Voisin et al.
Table II shows FSM, CFM and RCFM wavenumbers and HWHM damping. As already reported for silicon nanoparticles inside silica, there is good agreement between CFM and FSM. The main differences of CFM are: (1) nonzero damping and (2) "extra modes" as described in the following section. RCFM modes match some of the CFM modes not predicted by FSM.

To present CSM results, the measure of nanoparticle motion in Figs. 1 to 3 is \( \langle u^2 \rangle_p \), the mean squared displacement within the nanoparticle of the normalized vibrational mode displacement field as calculated using Eq. 4. In each case, \( \langle u^2 \rangle_p \) is plotted individually for each mode versus the mode’s wavenumber in cm\(^{-1}\). To make it easier to compare different materials and different sizes, the different \( \langle u^2 \rangle_p \) plots cover approximately the first two (SPH, l=0) pseudomodes.

Figure 4 shows individual plots for the separate cases of \( q \) and \( l \). Wavenumbers and HWHM of pseudomodes using CFM as listed in Tab. III are also indicated on the figure as arrows.

It is apparent that the interior of the nanoparticle is in motion for every CSM mode, unlike FSM wherein the nanoparticle would only vibrate at a discrete set of frequencies.

Relatively smooth dependence of \( \langle u^2 \rangle_p \) on frequency is seen for (TOR, l=1), (TOR, l=2) and (SPH, l=0) modes. The graph is much more complicated for the (SPH, l=1) and (SPH, l=2) cases. In these latter spheroidal modes, the motion is a mixture of longitudinal and transverse waves travelling at different speeds. Normal modes are forced to mix these two polarizations in order to satisfy boundary conditions at \( R = R_p \) and \( R = R_m \). Changing the boundary condition at \( R = R_m \) from zero traction to zero displacement doesn’t change the appearance of these plots.

Points in the (SPH, l≠0) plots clearly tend to cluster on two curves, with a few points lying in between. The (SPH, l≠0) plots consist of a longitudinal-like curve with one broad peak and a transverse-like curve with five peaks. CFM calculations also reveal this feature because some modes are broader.

In agreement with Voisin et al., Fig. 1 shows that Ag in BaO-P\(_2\)O\(_5\) has significant damping, but the nanoparticle’s damped pseudomodes are clearly visible. This probably explains why well resolved Raman peaks can be observed.

With the exception of "matrix modes" discussed in the following section, there is good agreement between the maxima of \( \langle u^2 \rangle_p \) from CSM and the wavenumbers and HWHM as predicted using CFM. Where CFM predicts modes where no \( \langle u^2 \rangle_p \) peaks appear, these also correspond to RCFM modes as discussed below. This and subsequent figures demonstrate the utility of CFM to predict the dominant frequencies at which the nanoparticle oscillates as well as their width.

### B. Extra Modes

The presence of the matrix leads to the appearance of some qualitatively new modes not given by FSM. We classify these as: (1) semi-rigid librational modes, which appear at the low frequency end of the (TOR, l=1) plots (near 5 cm\(^{-1}\) in Fig. 1). Both CFM and CSM confirm their presence. The zero frequency limit of FSM for (TOR, l=1) corresponds to rigid rotation. We therefore identify low frequency (TOR, l=1) modes as nearly rigid rotational oscillation. (2) semi-rigid rattling modes, also at the low frequency end of the (SPH, l=1) plots (near 3 cm\(^{-1}\) in Fig. 1), also confirmed by both CFM and CSM. The zero frequency limit of FSM for (SPH, l=1) corresponds to rigid rectilinear motion. We therefore identify low frequency (SPH, l=1) modes as nearly rigid translational oscillation. (3) "matrix modes" predicted by CFM but not apparent in the plots of \( \langle u^2 \rangle_p \) from CSM. These modes are well approximated by RCFM, which confirms their nature as motions of the matrix which do not significantly shake the nanoparticle. VCFM is a good approximation for the case of a heavier and more rigid matrix.

CFM roots were obtained numerically in this work. However, some exact calculations are possible for "matrix modes". As an example, for (SPH, l=0) modes, there is only one VCFM eigenfrequency given by \( \xi = 2\gamma \left( \sqrt{1 - \gamma^2} + i\gamma \right) \) (see Eq. (14') in Dubrovskiy et al.\(^{22}\)) and only one RCFM eigenfrequency given by \( \xi = i \) where \( \gamma = \nu^{m}/\nu^{l} \) and \( \xi = \omega R/\nu^{l} \). To our knowledge, this is the first report of Re(\( \omega \))=0 modes in such systems.
C. Pseudomode Damping

In the absence of the matrix, the nanoparticle will vibrate at frequencies $\omega_{\text{FSM}}^{F\text{SM}}$. Coupling of the nanoparticle to the matrix damps these pseudomodes. One way to get a qualitative feeling for this problem is to compare acoustic impedances. For plane sound waves in a fluid, acoustic impedance is density times speed of sound. Reflection at normal incidence from a planar interface is related to the difference of acoustic impedance between the two fluids. This concept also applies in general terms to acoustic waves in a solid (see Appendix C). When acoustic impedances for the nanoparticle $Z_p = \rho_p v_p$ and the matrix $Z_m = \rho_m v_m$ match, reflection of longitudinal sound waves is negligible. As the acoustic impedance mismatch increases, acoustic wave reflection increases leading to more pronounced nanoparticle modes. This is clearly seen in Fig. 2 where varying only the density of the matrix changes the locations of frequencies at which $\langle u^2 \rangle_p$ peaks. For low matrix mass density ($Z_p > Z_m$), $\langle u^2 \rangle_p$ peaks close to the FSM frequencies. For high matrix mass density ($Z_p < Z_m$), peaks appear close to the BSM frequencies. For matching impedances ($\rho_m \approx 2.24 \rho_{\text{BaO-P}_2\text{O}_5}$), oscillations are weak.

BaO-P$_2$O$_5$ is a heavy and rigid kind of glass.

Elastic parameters for Na at 300 K are from P. Ho et al.\cite{24} and directionally averaged to get sound speeds 1610 m/s and 3300 m/s. In this case $Z_p/Z_m \approx 0.182$.

Figure 3 shows the plots of $\langle u^2 \rangle_p$ from CSM. CFM mode wavenumbers and HWHM are shown as arrows. Peaks of $\langle u^2 \rangle_p$ are always narrow and close to BSM frequencies (not shown). CFM predicts additional much broader peaks which do not appear in $\langle u^2 \rangle_p$, but these are close to VCFM frequencies as given in Tab. III. Unlike a heavy nanoparticle in a light matrix, no additional low frequency mode corresponding to semi-rigid librational (TOR,1) or rattling (SPH,1) mode appears in the $\langle u^2 \rangle_p$ plots.

D. Na in BaO-P$_2$O$_5$ glass

This hypothetical case illustrates a soft nanoparticle in a hard matrix. Sodium is a very light and soft metal.

| mode | l | n | $\nu$ | $\Delta \nu$ |
|------|---|---|------|----------|
| SPH  | 0 | 0 | 4.6  | 3.2      |
|      | 1 | 0 | 0.0  | 3.1      |
|      | 1 | - | 0.0  | 7.9      |
|      | 2 | - | 7.9  | 4.4      |
|      | 2 | 0 | 2.9  | 2.3      |
|      | 1 | - | 4.1  | 10.4     |
|      | 2 | - | 11.9 | 5.0      |
| TOR  | 1 | 0 | 2.4  | 4.2      |
|      | 2 | 0 | 0.0  | 5.6      |
|      | 1 | - | 5.4  | 4.2      |

TABLE III: Wavenumber ($\nu$) and damping ($\Delta \nu$) in cm$^{-1}$ of modes of a BaO-P$_2$O$_5$ matrix surrounding a spherical cavity (VCFM) with radius $R_p = 4.9$ nm.
TABLE IV: Wavenumber (ν) and FWHM ( Δν) in cm⁻¹ of a matrix surrounding an infinitely rigid and heavy sphere (RCFM). Sphere radius is 3.4 nm.

| mode | l  | n  | SiO$_2$ ν | Δν  | GeO$_2$ ν | Δν  |
|------|----|----|---------|-----|--------|-----|
| SPH  | 0  | 0  | 0.0     | 9.3 | 0.0    | 5.4 |
|      | 1  | 0  | 7.6     | 12.2| 4.4    | 7.0 |
|      | 2  | 0  | 0.0     | 6.2 | 0.0    | 3.5 |
|      | 1  | 1  | 0.0     | 19.6| 0.0    | 11.3|
|      | 2  | 1  | 15.2    | 14.5| 8.8    | 8.3 |
| TOR  | 1  | 0  | 0.0     | 5.9 | 0.0    | 3.3 |
|      | 2  | 0  | 5.1     | 8.8 | 2.9    | 5.0 |

This example is chosen to show what happens when the elastic properties of the nanoparticle and the matrix are very similar. Low frequency Raman experiments on such systems reveal broad peaks whose Raman position scales inversely with nanoparticle size.

E. Si in SiO$_2$

Elastic parameters and mass density for silicon and silica are taken from our previous work$^{13,25,26}$ reveals broad peaks whose Raman position scales inversely with nanoparticle size.

In this paper, we will focus on CdS nanoparticles and show the influence of two different matrices. Introducing a thin intermediate layer between the nanoparticle and the matrix is a way to achieve this. Acoustic modes. Introducing a thin intermediate layer between the nanoparticle and the matrix is a way to achieve this.

Low-frequency Raman experiments on such systems$^{13,25,26}$ reveal broad peaks whose Raman position scales inversely with nanoparticle size. However, choosing the mass density and elastic parameters for this intermediate shell is a difficult task.

F. CdS

Many low-frequency Raman studies have been published for matrix embedded CdS$_x$Se$_{1-x}$ nanoparticles. Because of the different matrices used and varying nanoparticle composition, it is very difficult to address all of them here. In this paper, we will focus on CdS nanoparticles and show the influence of two different matrices. Low-frequency Raman spectra of CdS nanoparticles embedded in sol-gel silica have been reported by Othmani et al.$^{27}$ and Saviot et al.$^{28}$ GeO$_2$ embedded CdS nanoparticles were investigated by Tanaka et al.$^{29}$

Elastic parameters for CdS at 300 K are taken from Berlincourt et al.$^{30}$ and directionally-averaged as before to get sound speeds 1870 m/s and 4290 m/s. We use elastic constants measured at constant electric field and do not consider piezoelectric corrections. Mass density and sound speeds for amorphous GeO$_2$ are from Antoniou et al.$^{31}$

CSM $\langle u^2 \rangle_p$ plots and CFM results are presented in Fig. 4. In both cases $Z_p/Z_m \approx 1.6$ which is very close to the previous Si in SiO$_2$ system. GeO$_2$ having a smaller impedance than SiO$_2$ (even when using transverse sound speeds), one would expect the features of the GeO$_2$ embedded nanoparticles to be slightly more pronounced than the SiO$_2$ ones because the impedance mismatch is bigger. It turns out to be more complex. Modes having a strong longitudinal character follow this trend while those having a strong transverse character present more resolved low-frequency features for SiO$_2$. This is revealed by both the CFM and CSM calculations. Notably, in the SiO$_2$ matrix, both CSM and CFM show a sharp (TOR,l=1) rigid librational mode at 10.3 cm⁻¹. The hexagonal crystal structure and lack of inversion symmetry of CdS makes its electronic properties anisotropic even if the nanocrystal is a perfect sphere. So it is possible that this mode could be Raman active. Acoustic properties are anisotropic too, even if this paper works around this issue by performing a directional average. Rigid librations may therefore have the ability to couple to electronic degrees of freedom and modulate inelastic light scattering.

The only satisfactory way to explain the low-frequency Raman features is to couple the CSM approach with the
work done by Sirenko et al.\textsuperscript{14} on the interaction of the electronic excitations quantized in the confining potential of the nanoparticle with bulk-like acoustic phonons. The calculated Raman spectra should be further narrowed by taking into account the variation of the vibration amplitude inside the nanoparticle as a function of the vibration frequency.

G. Vibrational density of states

Free\textsuperscript{15} and weakly coupled\textsuperscript{33} nanoparticles are interesting objects because their vibrational density of states (VDOS) below the lowest FSM mode vanish. However, in our case both FSM and CFM have discrete mode spectra and do not reproduce the correct phonon density of states. Using CSM we calculated the VDOS. Note that this only involves finding the frequencies of the core-shell system. Amplitude normalization is not needed here.

\[
\frac{N(\nu)}{V} = \frac{1}{V} \int_0^\nu D(\nu') d\nu'
\]  

(5)

where \(V\) is the volume of the core-shell system.

The cumulative number of modes per unit volume up to wavenumber \(\nu\) (Eq. (6)) is plotted in Fig. 6 for the case of a silver nanoparticle embedded in a \(\text{BaO-P}_2\text{O}_5\) matrix. The lowest frequency for a given mode \((q,l)\) increases with \(l\). The numbers of TOR and SPH modes up to \(l=60\) had to be summed taking into account the \(2l+1\) degeneracy. In this way, the VDOS up to \(\nu = 15\ \text{cm}^{-1}\) for \(R_m/R_p = 10\) was obtained. Calculations for \(R_m/R_p = 3\) were also performed. Results are compared to the Debye model using matrix sound speeds (Eq. (6)).

\[
\frac{N_{\text{Debye}}(\omega)}{V} = \frac{1}{2\pi^2} \frac{1}{\nu L^3} \omega^3 - \frac{2}{\nu T^3} \omega^3
\]  

(6)

The presence of the nanoparticle doesn’t appreciably modify the VDOS, even for small \(R_m\).

VI. CONCLUSION

Within a continuum elastic approximation, the phonon spectrum of an isotropic spherical nanoparticle embedded in a macroscopic matrix can be calculated without approximation. This facilitates computations that require information about the phonon modes, and resolves the apparent contradiction involved in using free sphere vibrational modes to describe the mechanical oscillations of embedded nanoparticles.

Even though by necessity an object embedded in a macroscopic matrix must vibrate at every frequency, the vibration of a nanoparticle in a light and soft matrix is clearly dominated by FSM modes. This explains the success of FSM to reproduce the results of Raman scattering.
experiments on metal and semiconductor nanoparticles embedded in glasses.

CFM is demonstrated to accurately predict both the frequency and HWHM of pseudomodes of a matrix-embedded nanoparticle. New low frequency features corresponding to semi-rigid librational and rattling motions as a result of the restorative force of the matrix are clearly confirmed using both CFM and CSM. This points out the most serious limitation of FSM for embedded nanoparticles. Even so, FSM-predicted frequencies of pseudomodes turn out to be surprisingly accurate. It is the acoustic impedance mismatch between nanoparticle and matrix due both to density and speed of sound difference that allows dampening to be sufficiently slight that nanoparticles can "look free" in some light scattering experiments.

While the new (SPH,l=1) and (TOR,l=1) modes are not Raman active for an isotropic perfectly spherical nanoparticle, various imperfections can potentially allow these motions to modulate the polarizability of the nanoparticle and contribute to Raman and Brillouin spectra. However, in situations where elaboration methods allow relatively spherical nanoparticle growth, these new modes remain "invisible" in Raman and Brillouin experiments. "Matrix modes" are also present, but because they are mainly restricted to the matrix, they can’t be observed in experiments which are very often made under resonant conditions on the nanoparticle electronic transitions. Thus, the new qualitative features of the motion of embedded nanoparticles are not readily observable in experiments.

Size variation within a sample of nanoparticles causes a distribution of nanoparticle pseudomode frequencies. Sample characterization methods such as TEM have the ability to measure the extent of this size variation, but elaboration methods are normally limited in their ability to restrict the range of nanoparticle radius within a sample. This important effect "masks" whatever line broadening of the pseudomodes results from matrix embedding.

Taken together, every feature of these systems conspires to obscure experimental indications that the nanoparticles really are embedded in solid material as opposed to floating in a vacuum. Consequently the original 1882 Lamb FSM remains a powerful calculational tool for the description of nanoparticle vibrations.

Displacement fields using CFM are complex valued and also blow up exponentially with $R$. Also, the frequencies are complex valued. So these cannot be used as classical degrees of freedom to be quantized. CSM provides a rigorous foundation for more detailed theoretical studies since it is clear how it can be quantized. Work is in progress to apply this approach together with the proper description of the nanoparticle confined electronic levels in order to simulate the Raman spectrum of some systems.

**APPENDIX A: MODE ORTHOGONALITY**

The kinetic energy and potential energy of the system (assuming only mode $A$ is excited) are:

$$T_A(t) = \frac{1}{2}\rho(\vec{R}) \|\ddot{\vec{u}}_A(\vec{R}, t)\|^2 d^3\vec{R}$$  \hspace{1cm} (A1)

$$V_A(t) = \frac{1}{2} \sum_{ijkl} c_{ijkl} u_{Ai,j} u_{Ak,l} d^3\vec{R}$$  \hspace{1cm} (A2)

By conservation of energy $E_A = T_A(t) + V_A(t)$ cannot depend on time. Suppose now that two modes $A$ and $B$ ($\omega_A \neq \omega_B$) are simultaneously excited, so that

$$\vec{u}(\vec{R}, t) = \sin(\omega_A t) \vec{u}_A(\vec{R}) + \sin(\omega_B t) \vec{u}_B(\vec{R})$$  \hspace{1cm} (A3)

$T_{A+B}(t)$ is the kinetic energy due to the superposition of the two modes. Therefore,

$$T_{A+B}(t) = T_A(t) + T_B(t) + \omega_A \omega_B \cos(\omega_A t) \cos(\omega_B t) \int \rho \vec{u}_A \cdot \vec{u}_B d^3\vec{R}$$

$V_{A+B}(t)$ is the elastic potential energy due to the superposition of the two modes. So,

$$V_{A+B}(t) = V_A(t) + V_B(t) + \sin(\omega_A t) \sin(\omega_B t) \int c_{ijkl} u_{Ai,j} u_{Bk,l} d^3\vec{R}$$  \hspace{1cm} (A5)

With both modes excited, the energy is $E_{A+B}$. We next evaluate $E_{A+B} - E_A - E_B$. By energy conservation (since there are no body or traction forces or energy dissipation mechanisms) $E_A$, $E_B$ and $E_{A+B}$ must all be constant in time. Consequently,

$$\int \rho(\vec{R}) \vec{u}_A \cdot \vec{u}_B d^3\vec{R} = 0$$  \hspace{1cm} (A6)

$$\int c_{ijkl} u_{Ai,j} u_{Bk,l} d^3\vec{R} = 0$$  \hspace{1cm} (A7)

Equation (A6) was derived as equation (3.72) on page 39 of Trallero-Giner et al.

Each of Eq. (A6) and Eq. (A7) provides an orthogonality on nondegenerate normal modes of vibrations. For convenience, we choose to orthonormalize the normal modes as in Eq. (11). Within a degenerate subspace, Gram-Schmidt orthogonalization can be used with this inner product to generate a complete orthonormal basis of normal modes.
APPENDIX B: ENERGY EQUIPARTITION

Nanoparticle vibrations are very far from thermal equilibrium when a short pulse of laser light heats the nanoparticle to thousands of degrees. Conversely, many experiments are done with low incident laser beam intensities so that temperature is constant throughout the nanoparticle and surrounding matrix.

For a linear classical mechanical system in thermodynamic equilibrium, each degree of freedom has average energy $k_B T$. Here we consider the approximate applicability of this equipartition theorem to vibrations of the embedded nanoparticle.

The nanoparticle is not an isolated system because of its mechanical connection to the matrix, but if the density or speeds of sound are significantly different (between nanoparticle and matrix) then there may be in effect a poor impedance match at the interface so that vibrational energy cannot readily enter or exit the nanoparticle. In this case there is hope that the nanoparticle can be approximated as a nearly isolated mechanical system only weakly coupled to the matrix.

Removing the matrix, the normal vibrational "pseudomodes" of the nanoparticle can be indexed by $lm\bar{n}q$. The term "pseudomodes" emphasizes that they are not normal modes because of the non-isolation of the system. Three indices $l$, $m$ and $q$ are in common with the corresponding indices of modes of the core-shell system as a whole, $\bar{n}$ is the index for the nanoparticle pseudo-modes and $n$ is the index for normal modes of the entire core-shell system.

Assuming weak coupling, each pseudomode $lm\bar{n}q$ will have average kinetic energy $\frac{1}{2}k_B T$. The coupling to the matrix leads to thermal fluctuations both of amplitude and phase of the motion within the nanoparticle. As a result the motion of a single pseudomode has a widened band of frequencies.

We add up kinetic energies within the nanoparticle for all core-shell modes whose $\omega_{lmnq}$ is close to $\omega_{lm\bar{n}q}$ of the pseudomode. This gives a time average kinetic energy associated with the pseudomode:

$$\langle T_{lm\bar{n}q}\rangle_t = \sum_n \frac{1}{4} \omega_{lmnq}^2 (x_{lmnq}^2 + y_{lmnq}^2) M_p \langle u_{lmnq}^2 \rangle_p \quad (B1)$$

Since each core-shell mode has average energy $k_B T$, $x_{lmnq}^2 + y_{lmnq}^2$ equals $2k_B T/(M_{p+m}\omega_{lmnq}^2)$. Thus,

$$\sum_n \langle u_{lmnq}^2 \rangle_p \approx \frac{M_{p+m}}{M_p} \quad (B2)$$

where the summation over $n$ includes only such core-shell modes for which $\omega_{lm\bar{n}q}$ is close to a particular pseudomode frequency $\omega_{lm\bar{n}q}$. This is well satisfied for the cases we have checked.

Since normal modes are normalized with respect to Eq. and since the integrand of is non-negative, $\langle u_{lmnq}^2 \rangle_p \leq M_{p+m}/M_p$.

APPENDIX C: ACOUSTIC IMPEDANCE

Acoustic impedance for sound waves can be generalized to the situation of a spherical wave crossing a spherical surface at normal incidence. In this case the acoustic impedance is complex valued. In addition to density and speed of sound it also depends on frequency and the radius of the interface. When the interface radius is large compared to the wavelength the acoustic impedance again approaches density times speed of sound. See equation (5.11.12) on page 128 of L. E. Kinsler et al.25

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