Elastic vibrations of nanoparticles with the effects of surface stress and surface inertia

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Summary The elastic vibrations of nanoparticles have been studied theoretically within the frame of surface elasticity. Besides the effect of surface stress, the effect of surface inertia has also been taken into account in the model. The results have shown that both the surface stress and the surface inertia affect significantly the eigenfrequencies of nanospheres. Comparison with experiments has demonstrated the suitability of the model to characterize the elastic vibrations of nanoparticles on the continuum level.

INTRODUCTION

Elastic vibrations of nanoparticles are important to determine their mechanical properties and to understand their anomalous thermal and electrical properties. Numerous experimental studies, e.g., by low-frequency Raman Scattering technique and time resolved spectroscopy have been conducted on the elastic vibrations of nanoparticles [1,2]. Quite often a reasonable estimate for the eigenfrequencies is required which has often been obtained by Lamb's solution of the continuum elastic problem for a sphere.

However, the apparent elastic properties of nanoparticles have been revealed to be size or radius dependent in some experimental studies [2, 3]. Such size dependent elastic properties may affect the elastic vibrations of nanoparticles as has been indicated in some experiments [2, 3]. Given the high value of the surface-to-volume ratio, naturally one may speculate that size dependent elastic properties may be attributed to the surface effect. Therefore, the present authors are motivated to study the elastic vibrations of nanoparticles by surface elasticity since it has been demonstrated well for characterizing the surface effect in nanosystems [4-7].

PROBLEM FORMUATLION AND SOLUTION

Within the surface elasticity, the effect of surface elastic properties is captured by introducing the surface stress tensor that is related to the surface strain as $\sigma^s_{\alpha\beta} = \sigma^s_0\delta_{\alpha\beta} + \lambda^s\varepsilon_{\kappa\kappa}\delta_{\alpha\beta} + 2\mu^s\varepsilon_{\alpha\beta}$ with σ^s_0 being the residual surface stress, λ^s and μ^s being the surface Lame constants. In the case of elastic vibrations, the inertia effect of the surface may arise as well, which together with bulk mass density ρ may define an intrinsic length $l_m = \rho^s/\rho$ with ρ_s the surface mass density. According to Ref.[4], the motion equations are exactly the same as those in classical elasticity and for the nanospheres of radius b considered here can be expressed in terms of potential functions as

$$\nabla^2\varphi = \frac{1}{c_d^2}\frac{\partial^2\varphi}{\partial t^2}, \nabla^2\psi = \frac{1}{c_s^2}\frac{\partial^2\psi}{\partial t^2}, \nabla^2\chi = \frac{1}{c_s^2}\frac{\partial^2\chi}{\partial t^2} \tag{1}$$

with boundary conditions as follows

$$\sigma_{rr}(b,\theta,\phi) + \frac{\sigma^s_{\theta\theta}+\sigma^s_{\phi\phi}}{b} + \rho^s\frac{\partial^2 u_r}{\partial t^2} = 0, \tag{2a}$$

$$\sigma_{r\theta}(b,\theta,\phi) - \left(\frac{1}{b}\frac{\partial\sigma^s_{\theta\theta}}{\partial\theta} + \frac{1}{b\sin\theta}\frac{\partial\sigma^s_{\theta\phi}}{\partial\phi} + \frac{\sigma^s_{\theta\theta}-\sigma^s_{\phi\phi}}{b}\cot\theta\right) + \rho^s\frac{\partial^2 u_\theta}{\partial t^2} = 0, \tag{2b}$$

$$\sigma_{r\phi}(b,\theta,\phi) - \left(\frac{1}{b}\frac{\partial\sigma^s_{\theta\phi}}{\partial\theta} + \frac{1}{b\sin\theta}\frac{\partial\sigma^s_{\phi\phi}}{\partial\phi} + \frac{2}{b}\sigma^s_{\theta\phi}\cot\theta\right) + \rho^s\frac{\partial^2 u_\phi}{\partial t^2} = 0, \tag{2c}$$

In Eq (1), $c_d = \sqrt{(\lambda+2\mu)/\rho}$ and $c_s = \sqrt{\mu/\rho}$ are respectively the longitudinal and shear wave speeds. The general solutions can be expressed as $\varphi = \sum_{n,m} A_{nm}F_n(\omega/c_d r)P_n^m(\cos\theta)\exp[i(m\phi-\omega t)]$, $\psi = \sum_{n,m} B_{nm}F_n(\omega/c_s r)P_n^m(\cos\theta)\exp[i(m\phi-\omega t)]$, $\chi = \sum_{n,m} C_{nm}F_n(\omega/c_s r)P_n^m(\cos\theta)\exp[i(m\phi-\omega t)]$ at which F_n is the nth order spherical Bessel function of the first kind, P_n^m the associated Legendre function, A_{nm}, B_{nm} and C_{nm} constants to be determined, and ω the circular frequency. The displacement components can be obtained from the relation $\mathbf{u} = \nabla\varphi + \nabla(r\psi)\times\mathbf{e}_r + \nabla[\partial(r\chi)/\partial r] - r\nabla^2\chi\mathbf{e}_r$. The stress can also be obtained using Hook's law. Substitution of them into Eqs (2a-c) yields a linear system whose determinant should be zero so as to calculate the eigenfrequencies. Of

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particular interest is the vibration that splits into torsion mode and spherical mode, which has been utilized to interpret the low-frequency Raman shift and whose eigenfrequencies are respectively determined by

$$\frac{F_n(\zeta_2 b)-\zeta_2 b F_n'(\zeta_2 b)}{b}-\frac{\mu^s}{\mu b}\frac{[n(n+1)-2]F_n(\zeta_2 b)}{b}+\frac{\rho^s\omega^2 F_n(\zeta_2 b)}{\mu}=0 \quad \text{and} \quad |D_{ij}|=0 \tag{3}$$

where $\zeta_2=\omega/c_s$ and the lengthy expressions for $D_{ij}\ (i,j=1,2)$ are neglected here because of the limited space.

RESULTS AND DISCUSSIONS

To illustrate the effect of surface stress and inertia, we take $c_d=4247$ m/s, $c_s=1859$ m/s, $\rho=4820$ kg/m^3 for CdS nanoparticle and take l_m and $\lambda^s/\lambda=\mu^s/\mu=l_s$ as adjustable parameters. For different values of n, l_m and l_s, the lowest eigenfrequencies of the torsion mode have been calculated and presented in Fig.1. Evidently, both the surface stress and surface inertia affect the vibrations significantly for spherical radius less than several nanometers. According to Tanaka et al [1], the Raman frequency shifts can be attributed the second lowest eigenfrequency for n=0. So herein we have numerically calculated the Raman shift for n=0 as a function of the sphere radius within the surface elasticity. Results are plotted in Fig 2, where for comparison, the experimental results and those by classical elasticity have also been given. It can be seen that the results by surface elasticity with nonzero l_m and l_s agree best with the experimental ones. Thus one may conclude that the surface elasticity may capture well the elastic vibrations of nanoparticles and the Raman shift of low frequency can be well interpreted by accounting surface effect. It is noted that although surface elasticity has been widely used to study the mechanical behavior of nanosystems, how to experimentally determine the surface parameters like the surface Lame constants has seldom been discussed. Raman spectroscopy may offer a good choice since it is non-destructive. However, more comparisons with experiments may be necessary and how to extract the surface properties easily from the method still requires further work.

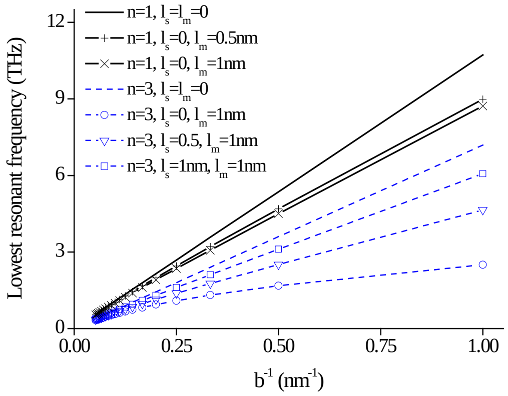

Fig.1 Resonant frequency for torsion mode;

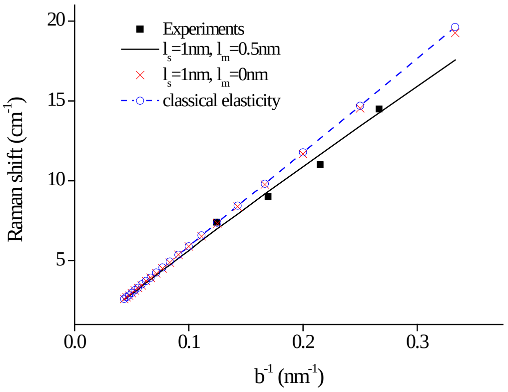

Fig.2 Comparison of Raman shift by different methods

CONCLUSIONS

In summary, the elastic vibration of a nanosphere has been studied within the surface elasticity model. The effect of surface elastic property and surface inertia on the resonant frequencies of nanospheres can be significant. Furthermore, the surface-elasticity based vibration can be used to interpret the low-frequency Raman scattering better than that based on the classical elasticity.

References

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