Damping by bulk and shear viscosity for confined acoustic phonons of a spherical virus in water

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Abstract. A sphere-like virus in water is modeled as a homogeneous isotropic elastic continuum sphere in contact with an infinite viscous compressible Newtonian fluid. The frequencies and damping of the confined vibrational modes of the sphere are calculated for the material parameters of a virus in water. While the effects of viscosity are found to be negligible for a virus-like sphere of macroscopic size, for nanoscale viruses both the frequency and damping of the vibrational modes are significantly affected by the viscosity of the water. Furthermore, both shear viscosity and bulk viscosity play an important role.

Confined acoustic phonons in nanostructures are mechanical vibrations whose frequency is on the order of the speed of sound divided by a typical length of the structure. For a nanoparticle floating in a liquid, vibrational energy is gradually lost due to radiation of sound waves into the surrounding liquid, resulting in damped modes. Nanoparticles in a liquid can have their vibrations observed by pulsed laser experiments\(^1\) and also by light scattering techniques.\(^2\)

The classical mechanical problem of finding the vibrational frequencies of a free, isotropic, homogeneous, continuum sphere was first solved by Lamb.\(^3\) The only parameters required are the sphere radius, density and speeds of sound in the bulk material. The vibrations are undamped and therefore can be said to be “confined” within the nanoparticle, in contrast to travelling wave phonon modes in a bulk solid.

It is frequently the case that nanoparticles are synthesized so as to be embedded in a solid matrix, for example silver in silica. In this case, the nanoparticle cannot vibrate in isolation due to the mechanical connection to the matrix. Even so, the presence of at least a moderate impedance mismatch for sound waves travelling across the interface between the nanoparticle and the matrix is sufficient to cause a significant back-reflection of the sound waves and, in this way, “confine” the phonon modes within the nanoparticle. However, the acoustic energy will gradually leak out into the matrix. Despite this, it is traditional to describe the damped vibrations of the nanoparticle as “confined” acoustic phonons.

The solution to the classical mechanical problem of an isotropic homogeneous continuum sphere embedded in an elastic matrix has been presented by Dubrovskiy.\(^4\) There are seven parameters: radius, two densities and four speeds of sound. The situation of a nanoparticle embedded in a liquid medium could plausibly be approached as a special case of the Dubrovskiy solution. Liquids have zero transverse sound speed. However, a physical property of the liquid that would be ignored in such a calculation is the viscosity. The effects of viscosity...
on vibrational modes are significant for all structures with nanoscale dimensions (100 nm or smaller).[5] However, these effects are negligible for microscale and larger structures.

Initial interest in the vibrational modes of viruses was motivated by the possibility of using ultrasound waves in resonance with these modes in order to destroy viruses in a living host.[6] There is a report of such a vibrational mode being observed in M13 (cylindrical) viruses using Raman scattering.[7] A rough theoretical estimate of the frequency of these modes was initially made by considering the virus as a free elastic sphere while ignoring the effect of the liquid solvent.[6] The effect of the surrounding water on the vibrational modes of a virus (or related biological structure) was considered later.[8, 9, 10, 11] However, these works all treated water as an elastic medium with zero transverse speed of sound and ignored the viscosity. The appearance of the effects of viscosity on nanoscale vibrations has previously been pointed out for the situation of a liquid drop as a model for a virus.[6] Viscosity of the solvent was explicitly taken into account but only for torsional modes in an early article pointing out the relevance of the study of vibrations for biological structures.[13]

The capsids of sphere-like viruses all show underlying icosahedral symmetry.[14] Some examples of icosahedral viruses are: papilloma virus, nudarelia capensis beta virus, poliovirus, satellite tobacco mosaic virus, tomato bushy stunt virus, southern bean mosaic virus, human rhinovirus 14, satellite panicum mosaic virus, and tobacco necrosis virus. The approximation of treating these viruses as perfect spheres is only justifiable for the lowest-lying acoustic phonon modes, which are the only ones that we discuss in this work. It is also an approximation to regard a virus as a homogeneous object, since it has internal structure. Finally, the actual elastic properties of the material of a virus is not well known, and cannot be assumed with certainty to be isotropic either.

Consider the sphere to be of density $\rho_p$ with isotropic elasticity so that its longitudinal and transverse speeds of sound are $v_{Lp}$ and $v_{Tp}$, respectively. The density of the liquid matrix is $\rho_m$ and the speed of longitudinal sound waves in the liquid is $v_{Lm}$. $v_{Tm}$ is zero.

Vibrational modes of a homogeneous isotropic sphere can be classified as torsional (TOR) or spheroidal (SPH).[3] Modes can be furthermore classified by the integer angular momentum number $\ell \geq 0$ and the angular momentum $z$-component $m$ where $-\ell \leq m \leq \ell$. There is no variation of frequency with $m$. Therefore, in what follows we consider the $m = 0$ case only.

Using the values of the material constants (from Talati et al.[8]) presented in Table 1, we have calculated complex-valued mode frequencies for the case of a homogeneous spherical virus in water. The results are presented in Figures 1 to 3, showing the variation of the mode frequencies with virus diameter. The strong variation as diameter varies clearly indicates the importance of viscosity. In the absence of viscosity, the dimensionless frequency would not vary with diameter.

Figure 1 shows the vibrational frequencies of (SPH, $\ell = 0$) modes, or breathing modes. For these modes, the mechanical vibration is purely radial, emanating from the geometric center of the virus. Such vibrational modes of nanoscale particles can be excited and detected using femtosecond pulsed laser experiments in which an initial brief laser pulse is used to rapidly heat

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|          | virus | H$_2$O |
|----------|-------|--------|
| $\rho$   | kg/m$^3$ | 1210  | 1000  |
| $v_L$    | m/s   | 1817  | 1498  |
| $v_T$    | m/s   | 915   | 0     |
| $\mu$    | Pa-s  | 0     | 0.00089 |
| $\zeta$  | Pa-s  | 0     | 0.00215[12] |

Table 1. Material constants used for Figures 1-3.
Figure 1. (In color online) Dimensionless vibrational mode frequency \( \xi = \omega R / v_{LP} \) is plotted versus virus diameter, \( 2R \). The solid lines (red online) show \( \text{Re}(\xi) \). The hatched bands surrounding the solid lines (green or blue online) extend from \( \text{Re}(\xi) - \text{Im}(\xi) \) to \( \text{Re}(\xi) + \text{Im}(\xi) \). The frequencies shown are for (SPH, \( \ell = 0 \)) modes of a virus in water. The black cross-hatched region in the top left is where mode frequency exceeds the limit for which these calculations are reliable.

Figure 2. As in Figure 1, except showing \( \eta = \omega R / v_{TP} \) for (SPH, \( \ell = 1 \)) modes.

Figure 3. As in Figure 1, except showing \( \eta = \omega R / v_{TP} \) for (SPH, \( \ell = 2 \)) modes.

the nanoparticle and thus lead to radial oscillations. Up to now, this has not been accomplished in viruses.

Figure 2 shows the vibrational frequencies of (SPH, \( \ell = 1 \)) modes, or dipolar modes. Based on symmetry arguments, it is anticipated that such modes have the ability to absorb infrared radiation.\(^{[15]}\) However, an additional requirement for these modes to be infrared active is the presence of a permanent inhomogeneous charge distribution within the nanoparticle.\(^{[16]}\) Spectral features in experimental terahertz absorption spectra attributed to (SPH, \( \ell = 1 \)) confined acoustic phonons in TiO\(_2\) nanopowders have been recently reported.\(^{[16]}\) However, up to now, there has been no report of terahertz absorption spectral features associated with confined acoustic phonons in viruses.

Figure 3 shows the vibrational frequencies of (SPH, \( \ell = 2 \)) modes, or quadrupolar modes. Based on symmetry arguments,\(^{[15]}\) such modes have the ability to inelastically scatter photons in experiments of the low frequency Raman or Brillouin type. The upshift or downshift in the frequency of the scattered photon corresponds to the frequency of the quadrupolar acoustic phonon mode. The same symmetry arguments predict the (SPH, \( \ell = 0 \)) modes are Raman active as well, but the intensity of Raman scattering is experimentally found to be weaker. Low frequency Raman scattering from acoustic phonons in metal and semiconductor nanoparticles is well known. However, up to now, there has been no report of experimental observation of inelastic light scattering from a sphere-like virus. Interestingly, there has been an experimental report of spectral features in low frequency Raman scattering for rod-like viruses which were attributed to confined acoustic phonons corresponding to the natural modes of vibration of an infinite free cylinder.\(^{[7]}\)
The applicability of all of the calculations reported here is limited to frequencies for which the local deterministic continuum hydrodynamic description of water is valid.[17] The viscosity may only be regarded as a frequency-independent quantity for wavevector \( q \) below 2 \( \text{nm}^{-1} \). Since \( \omega = cq \) and \( c = 1498 \text{ m/s} \) for water, the limiting frequency is approximately \( 3.0 \times 10^{12} \text{ rad/s} \) (or 16 \( \text{cm}^{-1} \)). Above this, the viscous coefficients of water become \( q \)-dependent. In each of the figures, there is a cross-hatched black region in the top left corner corresponding to mode frequencies above this limit.

It is clear that viscosity is an important consideration for virus-like nanoparticles in water. However the qualitative effects show remarkable variety. Frequencies are normally shifted downwards from their values in the absence of viscosity. However, the effect on the damping of the mode can be either to extend the lifetime or to shorten it. Although we do not separately show the effects of shear and bulk viscosity here, previous work[5] showed that both coefficients have comparably significant effects, although in different situations. It is worth pointing out that viscosity is strongly temperature dependent, permitting the degree of viscosity effects to be conveniently controlled in an experiment. Certainly, viscosity must be taken into consideration as efforts to experimentally identify confined acoustic phonons in viruses and other biological nanostructures continue.

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References
[1] Hartland G V 2006 Annu. Rev. Phys. Chem. 57 403
[2] Penciu R S, Kriegs H, Petekidis G, Fytas G and Economou E N 2003 J. Chem. Phys. 118 5224
[3] Lamb H 1882 Proc. London Math. Soc. 13 189
[4] Dubrovskiy V A and Morochnik V S 1981 Earth Physics 17 494
[5] Saviot L, Netting C H and Murray D B 2007 J. Phys. Chem. B 111 7457
[6] Ford L H 2003 Phys. Rev. E 67 051924
[7] Tsen K T, Dykeman E C, Sankey O F, Lin N T, Tsen S W D and Kiang J G 2006 Virology Journal 3 79
[8] Talati M and Jha K 2006 Phys. Rev. E 73 011901
[9] Balandin A A and Fonoberov V A 2005 J. Biomed. Nanotech. 1 90
[10] Fonoberov V A and Balandin A A 2004 phys. stat. sol. (b) 241 R67
[11] Sireno Y M, Stroscio M A and Kim K W 1996 Phys. Rev. E 53 1003
[12] Litovitz T A and Carnevale E H 1955 J. Appl. Phys. 26 816
[13] De Gennes P G and Papoilar M 1969 Polarisation mati`ere et rayonnement ed Soci´et´e Fran¸caise de Physique (Paris: Presses Universitaires de France) p 243
[14] Marzec C J and Day L A 1993 Biophys. J. 65 2559
[15] Duval E 1992 Phys. Rev. B 46 5795–5797
[16] Murray D B, Netting C H, Saviot L, Pighini C, Millot N, Aymes D and Lin H L 2006 J. Nanoelec. Optoelec. 1 92
[17] Monaco G, Cunsolo A, Ruocco G and Sette F 1999 Phys. Rev. E 60 5505

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