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Phonon scattering cross section of polydispersed spherical nanoparticles

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An approximate analytical solution is proposed to estimate the phonon scattering cross section of polydispersed spherical nanoparticles. Using perturbation of the Hamiltonian due to differences in mass and bond stiffness between a host medium and a spherical nanoparticle, an analytical solution is obtained for the scattering cross section in the Rayleigh limit when the size parameter approaches zero. In the geometrical scattering limit, when the size parameter approaches infinity, the van de Hulst approximation for anomalous diffraction is used to estimate the scattering cross section as a function of acoustic impedance mismatch between the host medium and the spherical nanoparticle. Finally, these two limiting cases are bridged by a simple expression to estimate the scattering cross section for intermediate values of the size parameter. Using this, the scattering cross section for a polydispersed distribution of spherical nanoparticles was also estimated as a function of the parameters defining the statistical size distribution. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Electromagnetic wave scattering by spherical particles has been widely studied and thoroughly reviewed.[1,2] However, acoustic wave scattering in solids due to spherical particles has drawn relatively less attention. Due to recent advances in material synthesis, it is possible to incorporate spherical nanoparticles in a material with sufficient control on their size. One example is the quantum dot superlattice.[3,4] Thermal transport in the materials due to spherical nanoparticles is particularly important in thermoelectric device applications,[5,6] which requires low thermal conductivity for efficient operation. Therefore, we propose an approximate analytical expression to calculate phonon scattering cross section of spherical nanoparticles. This analytical solution will also be useful to extract important parameters for designed materials.

Ying and Truell[7] developed a so-called acoustic Mie theory, in which they solved the acoustic wave equations to derive the scattering cross section of spherical particles in solids. When the incoming wave is scattered by the spherical particle, just like Mie theory of electromagnetic waves,[1,2] one subsequently considers three separate waves. The first wave is an unimpeded incident plane wave, the second is a spherical wave scattered by the particle, and the third is excited inside the particle.[7] Outside of the spherical particle, the first two waves are superposed due to the linear and homogeneous nature of the wave equation. Although the solution process looks straightforward, the resulting solution is mathematically complicated. Therefore, computations are usually necessary to solve the scattering cross section due to a spherical particle. It is, therefore, difficult to establish distinct relationships between scattering cross section and the various scattering parameters. Despite this, the acoustic Mie theory has served as a useful method to estimate the phonon mean-free path due to scattering by spherical nanoparticles in solids.[8–10]

Due to the need of a simple expression for scattering cross section, Majumdar[11] proposed

$$\sigma = \pi R^2 \left(\frac{\chi^4}{\chi^4 + 1} \right), \tag{1}$$

where σ denotes scattering cross section, R is the radius of the spherical nanoparticle, and χ is the size parameter, defined as $\chi = qR$, where q is the incoming wave vector. This equation basically connects the two extremes of scattering cross section versus frequency. When the size parameter approaches zero ($\chi \ll 1$), the scattering cross section obeys Rayleigh law, which varies as frequency to the fourth power. At the other limit, where the size parameter reaches infinity ($\chi \to \infty$), the scattering cross section is independent of frequency. Although this method does not capture the transition between those two extremes, where σ usually shows oscillatory behavior, this could be acceptable as a first-order approximation.

In this study, we will further refine this idea and investigate the effects of differences in mass and bond stiffness on scattering. Here, again, analytical solutions are obtained in those two extremes and connected with a simple formula.[11,12] We also considered the case of polydispersion of spherical nanoparticles. In the Rayleigh scattering regime, Klemens' expression for point defect[13,14] based on quantum-mechanical perturbation theory has been extended to treat a spherical nanoparticle. Differences in mass and force constant between the host medium and the spherical nanoparticle give rise to perturbations in kinetic and potential energy of the Hamiltonian. In the geometrical scattering regime, which is the other extreme, van de Hulst's approximation[2] for electromagnetic wave scattering is adopted to treat acoustic wave scattering.

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II. THEORETICAL ANALYSIS

To study phonon transport in solids, one generally uses the Boltzmann transport equation, which is given as

$$\frac{\partial N}{\partial t} + \boldsymbol{\upsilon} \cdot \nabla N = \left(\frac{\partial N}{\partial t}\right)_{\text{sct}}, \tag{2}$$

where $N(r,p,t)$ is the statistical distribution function for phonons, which varies with time t, particle position vector r, and momentum vector p. υ is the group velocity. The terms on the left side are called drift terms, whereas that on the right is the scattering term. The relaxation time approximation assumes the scattering term as

$$\left(\frac{\partial N}{\partial t}\right)_{\text{sct}} = \frac{N_0 - N}{\tau_{\text{DR}}} = -\frac{n}{\tau_{\text{DR}}}, \tag{3}$$

where τ_{DR} is the relaxation time and n is the deviation from equilibrium. For scattering by particles or impurities, the relaxation time is related to the scattering cross section as

$$\tau_{\text{DR}} = \frac{1}{\eta \upsilon \sigma}, \tag{4}$$

where η is concentration. Therefore, from now on, the derivation will be focused on how to derive the scattering cross section in Eq. (3).

A. Rayleigh scattering regime

The scattering of lattice waves by point defects was treated by perturbation theory by Klemens,[13,14] using which he proposed a phonon relaxation time due to point defects. Later he extended this theory for a platelet-shaped object.[15] Here we further extend this theory in the case of spherical nanoparticles. Usually the analytical expressions of the relaxation time are derived from time-dependent perturbation theory[16] which gives the transitional probability from one state to another. The perturbation theory captures the physics behind the phonon scattering as follows. Phonons represent the quantized energy of a lattice wave,[17–19] and the lattice can generally be modeled as a spring-mass system. Therefore, a particle can scatter a phonon when (a) its mass is different than that of the host material, and/or (b) its spring constant, i.e., force constant, is not equal to that of the host material.[13,14] This change in mass and/or spring constant gives rise to perturbed kinetic and/or potential energy of the Hamiltonian. Therefore, the perturbed Hamiltonian, H', can be expressed as

$$H' = \sum_{\mathbf{q},\mathbf{q}'} c_2(\mathbf{q},\mathbf{q}') a^*(\mathbf{q}') a(\mathbf{q}), \tag{5}$$

where $\mathbf{q}$ and $\mathbf{q}'$ are the incoming and scattered wave vectors, respectively. c_2 is a coefficient appearing in perturbation Hamiltonian due to mixed terms of $a^*(\mathbf{q}')a(\mathbf{q})$, where $a(\mathbf{q})$ and $a^*(\mathbf{q}')$ denote phonon annihilation and creation operators, respectively. The relaxation time due to nanoparticle is expressed as[13–15]

$$\frac{1}{\tau_{\text{DR}}} \approx \frac{V}{(2\pi)^2 M^2} \int dS_{\omega'} \frac{|c_2(\mathbf{q},\mathbf{q}')|^2}{\omega^2 \upsilon} \left(1 - \frac{n'}{n}\right), \tag{6}$$

where M is the mass of the host material and V is the volume of a crystal. ω denotes the angular frequency of the lattice wave and n is the deviation from equilibrium. $dS_{\omega'}$ is the surface element in the Brillouin zone with a constant ω'.

1. Mass difference scattering

Now, we are going to describe how to get c_2 in Eq. (6) in the case of a spherical nanoparticle. We first consider the case where the mass of the spherical nanoparticle differs from its host medium. Then, the perturbed Hamiltonian is

$$H' = \frac{1}{2} \sum_{\mathbf{x}} \Delta M \dot{u}(\mathbf{x})^2, \tag{7}$$

where ΔM is the mass difference between the host and the spherical nanoparticle, $u(x)$ is the displacement of atom in its equilibrium position, and $\dot{u}(x)$ is the velocity of the displacement. Therefore, Eq. (7) represents the case when the mass difference between the host and the nanoparticle affects the kinetic energy of the Hamiltonian, summed over the spherical nanoparticle sites. The displacement of atom, $u(x)$, is represented as

$$\begin{aligned} u(\mathbf{x}) &= \frac{1}{\sqrt{G}} \sum_{\mathbf{q}} \boldsymbol{\varepsilon} b(\mathbf{q}) \exp[i\mathbf{q}\cdot\mathbf{x} + i\omega(\mathbf{q})t] \\ &= \frac{1}{\sqrt{G}} \sum_{\mathbf{q}} \boldsymbol{\varepsilon} a(\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{x}), \end{aligned} \tag{8}$$

where G is the number of lattice sites in the crystal, b is amplitude of the displacement, $a(\mathbf{q})$ is annihilation operator, and $\boldsymbol{\varepsilon}$ is a unit vector describing polarization. Therefore, plugging Eq. (8) in Eq. (7) and comparing this with Eq. (5) results in the following equation:

$$\begin{aligned} c_2(\mathbf{q},\mathbf{q}') &= -\frac{\Delta M}{2G} \sum_{\mathbf{x}} \omega\omega'(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}') \exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}] \\ &= -\frac{\Delta M}{2G} \sum_{\mathbf{x}} \omega\omega'(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}') \exp(i\mathbf{Q}\cdot\mathbf{x}). \end{aligned} \tag{9}$$

To evaluate Eq. (9), the summation over lattice points indicating the spherical nanoparticle needs to be calculated. The coordinates to evaluate Eq. (9) are shown in Fig. 1(a) where β and θ are the polar and azimuthal angle, respectively,

$$\mathbf{Q}\cdot\mathbf{x} = |\mathbf{Q}| r \cos\beta, \tag{10}$$

$$\begin{aligned} &\sum_{\mathbf{x}} \exp(i\mathbf{Q}\cdot\mathbf{x}) \\ &= \frac{1}{\delta^3} \int_0^{\pi} \int_0^{2\pi} \int_0^{R} \exp(i|\mathbf{Q}| r\cos\beta) r^2 \sin\beta \, dr d\theta d\beta \\ &= \frac{4\pi R^3}{\delta^3 (|\mathbf{Q}|R)^3} [\sin|\mathbf{Q}|R - |\mathbf{Q}|R\cos(|\mathbf{Q}|R)], \end{aligned} \tag{11}$$

where δ^3 is the atomic volume. This term appears in Eq. (11) to consider the discrete nature of atoms composed of the

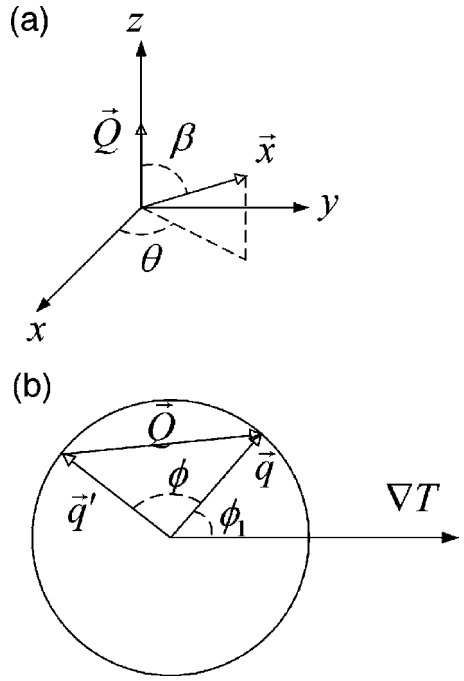

FIG. 1. (a) Coordinates to evaluate $\mathbf{Q}$ and $\mathbf{x}$ used in Eq. (19). β and θ are the polar and azimuthal angles, respectively. (b) Coordinates showing the wave vector with respect to the temperature gradient, ∇T. ϕ_1 and ϕ_2 are the angles of the incoming wave vector, $\mathbf{q}$, and the scattered wave vector, $\mathbf{q}'$, with respect to temperature gradient, respectively. ϕ is the difference between ϕ_1 and ϕ_2.

spherical nanoparticle. Before evaluating Eq. (6) in the case of the spherical nanoparticle, the surface element with constant ω' is written as

$$dS_{\omega'} = |\mathbf{q}'|^2 \sin\phi_2 d\phi_2 d\Theta = 2\pi|\mathbf{q}'|^2 \sin\phi_2 d\phi_2, \tag{12}$$

where ϕ_1 and ϕ_2 are the angles of the incoming wave vector, $\mathbf{q}$, and the scattered wave vector, $\mathbf{q}'$, with respect to temperature gradient respectively. ϕ is the difference between ϕ_1 and ϕ_2. Θ is the angle between the projection of $\mathbf{q}$ and $\mathbf{q}'$ on the xy plane. Before putting Eqs. (11) and (12) into Eq. (6), we make the approximation that the last term on the right-hand side in Eq. (6) is unity, i.e., $(1-n'/n)\approx 1$. In the phonon Boltzmann transport equations with relaxation time approximation, i.e., Eqs. (2) and (3), n is proportional to direction cosine with respect to temperature gradient.[13–15] Now Eq. (6) is written as

$$\begin{aligned}\frac{1}{\tau_{\mathrm{DR}}} &= \frac{(8\pi)R^6}{V}\left(\frac{\Delta M}{2M}\right)^2 \int [\omega\omega'(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}')]^2 \\ &\quad \times \frac{[\sin|\mathbf{Q}|R - |\mathbf{Q}|R\cos(|\mathbf{Q}|R)]^2}{(|\mathbf{Q}|R)^6\omega^2 v_g}|\mathbf{q}'|^2 \sin\phi_2 d\phi_2 \\ &= \frac{\alpha^2(8\pi)R^6}{V}\left(\frac{\Delta M}{2M}\right)^2 \frac{\omega^4}{v_g^3}\int \frac{[\sin|\mathbf{Q}|R - |\mathbf{Q}|R\cos(|\mathbf{Q}|R)]^2}{(|\mathbf{Q}|R)^6} \\ &\quad \times \sin\phi_2 d\phi_2. \end{aligned} \tag{13}$$

Here let the trigonometric ratio, $(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}')$, be α. Now to solve the integration, let the wave vector be

$$|\mathbf{Q}| = |\mathbf{q}|\sqrt{2(1-\cos\phi)}. \tag{14}$$

This is obvious from Fig. 1(b).

$$\frac{1}{\tau_{\mathrm{DR}}} = \frac{\alpha^2\pi}{V}\left(\frac{\Delta M}{2M}\right)^2 \frac{\omega^4}{v^3}\frac{R^6}{(qR)^6}F(|\mathbf{q}|R), \tag{15}$$

where

$$F(|\mathbf{q}|R) = \int_0^\pi \frac{[\sin(|\mathbf{q}|R\sqrt{2(1-\cos\phi)}) - |\mathbf{q}|R\sqrt{2(1-\cos\phi)}\cos(|\mathbf{q}|R\sqrt{2(1-\cos\phi)})]^2}{8(|\mathbf{q}|R)^6(1-\cos\phi)^3}\sin\phi d\phi. \tag{16}$$

Equation (16) was solved by MATLAB (Ref. 20) using symbolic integration. The result is as follows:

$$F(|\mathbf{q}|R) = \frac{\cos(4|\mathbf{q}|R) - 1 + (4|\mathbf{q}|R)\sin(4|\mathbf{q}|R)}{16} + 2(|\mathbf{q}|R)^2\left[(|\mathbf{q}|R)^2 - \frac{1}{4}\right]. \tag{17}$$

Therefore, the final form of Eq. (15) is

$$\frac{1}{\tau_{\mathrm{DR}}} = \frac{\alpha^2}{V}\left(\frac{\Delta M}{2M}\right)^2 \frac{\omega^4}{v^3}\left(\frac{4\pi R^3}{3}\right)^2\left\{\frac{9[\cos(4|\mathbf{q}|R) - 1 + (4|\mathbf{q}|R)\sin(4|\mathbf{q}|R)]}{16^2(|\mathbf{q}|R)^6} + \frac{9}{8(|\mathbf{q}|R)^4}\left[(|\mathbf{q}|R)^2 - \frac{1}{4}\right]\right\}. \tag{18}$$

2. Force constant difference scattering

If the force constant of the spherical nanoparticle differs from its host medium, the perturbed Hamiltonian is[13]

$$H' = \frac{1}{2}\sum_{\mathbf{x}}\sum_{\mathbf{l}} \langle \Delta K_{\parallel}\{\mathbf{l}\cdot[u(\mathbf{x}) - u(\mathbf{x}-\mathbf{l})]\}^2 + \Delta K_{\perp}\{\mathbf{l}\times[u(\mathbf{x}) - u(\mathbf{x}-\mathbf{l})]\}^2\rangle, \tag{19}$$

where K denotes the force constant of the host medium, ΔK is the force constant difference between the host and the spherical nanoparticle, and $\mathbf{l}$ is the unit vector in the direction of the linkage. The subscripts $\parallel$ and $\perp$ denote the directions parallel and perpendicular to the linkage, respectively. Therefore, the first and the second terms in Eq. (19) represent relative displacements parallel and perpendicular to the linkages, respectively. If we expand the Eq. (19) as

$$H' = \frac{1}{2}\sum_{\mathbf{x}}\sum_{\mathbf{l}}\left\langle \begin{array}{l} \Delta K_{\parallel}\left\{\begin{array}{l} 2[\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x})] - [\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x}+\mathbf{l})] \\ -[\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x}-\mathbf{l})] \end{array}\right\} \\ +\Delta K_{\perp}\left\{\begin{array}{l} 2[\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x})] - [\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x}+\mathbf{l})] \\ -[\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x}-\mathbf{l})] \end{array}\right\} \end{array}\right\rangle \tag{20}$$

then there is no need to do "long wave approximations" as Klemens did.[13] With Eq. (8), the first and the second terms in the parenthesis in Eq. (20) can be written as

$$\begin{aligned} &2[\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x})] \\ &\quad -[\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x}+\mathbf{l})] - [\mathbf{l}\cdot u(\mathbf{x})][\mathbf{l}\cdot u(\mathbf{x}-\mathbf{l})] \\ &= \frac{1}{G}\sum_{\mathbf{q},\mathbf{q}'}(\boldsymbol{\varepsilon}\cdot\mathbf{l})(\boldsymbol{\varepsilon}'\cdot\mathbf{l})a^{*}(\mathbf{q}')a(\mathbf{q})\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}] \\ &\quad \times\left[4\sin^2\left(\frac{\mathbf{q}'\cdot\boldsymbol{\delta}\mathbf{l}}{2}\right)\right], \end{aligned} \tag{21}$$

$$\begin{aligned} &2[\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x})] - [\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x}+\mathbf{l})] \\ &\quad -[\mathbf{l}\times u(\mathbf{x})][\mathbf{l}\times u(\mathbf{x}-\mathbf{l})] \\ &= \frac{1}{G}\sum_{\mathbf{q},\mathbf{q}'}(\mathbf{l}\times\boldsymbol{\varepsilon})\cdot(\mathbf{l}\times\boldsymbol{\varepsilon}')a^{*}(\mathbf{q}')a(\mathbf{q})\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}] \\ &\quad \times\left[4\sin^2\left(\frac{\mathbf{q}'\cdot\boldsymbol{\delta}\mathbf{l}}{2}\right)\right], \end{aligned} \tag{22}$$

where δ is distance between the nearest atoms. By comparison with Eqs. (21) and (22) and Eq. (5), c_2 can be deduced as

$$\begin{aligned} c_2(\mathbf{q},\mathbf{q}') &= \frac{2}{G}\sum_{\mathbf{x}}\sum_{\mathbf{l}}\left[\begin{array}{l}\Delta K_{\parallel}(\boldsymbol{\varepsilon}\cdot\mathbf{l})(\boldsymbol{\varepsilon}'\cdot\mathbf{l}) \\ +\Delta K_{\perp}(\mathbf{l}\times\boldsymbol{\varepsilon})\cdot(\mathbf{l}\times\boldsymbol{\varepsilon}')\end{array}\right] \\ &\quad\times\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}]\sin^2\left(\frac{\mathbf{q}'\cdot\boldsymbol{\delta}\mathbf{l}}{2}\right). \end{aligned} \tag{23}$$

Here we make the approximation that the parallel force constant is the same as the perpendicular force constant. We let the trigonometric ratio $(\boldsymbol{\varepsilon}\cdot\mathbf{l})$, $(\boldsymbol{\varepsilon}'\cdot\mathbf{l})$, or $(\mathbf{l}\times\boldsymbol{\varepsilon})\cdot(\mathbf{l}\times\boldsymbol{\varepsilon}')$ be α. Equation (23) can be written as

$$\begin{aligned} c_2(\mathbf{q},\mathbf{q}') &= \frac{4\alpha^2}{G}\sum_{\mathbf{x}}\sum_{\mathbf{l}}\Delta K\sin^2\left(\frac{\mathbf{q}'\cdot\boldsymbol{\delta}\mathbf{l}}{2}\right)\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}] \\ &= \frac{12\alpha^2}{G}\sum_{\mathbf{x}}\Delta K\sin^2\left(\frac{\mathbf{q}'\cdot\boldsymbol{\delta}\mathbf{l}}{2}\right)\exp[i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}], \end{aligned} \tag{24}$$

where the three directions of $\mathbf{l}$ are considered. Now using this equation into the Eq. (6) and following the same procedures as we did for mass difference scattering results in

$$\begin{aligned} \frac{1}{\tau_{\mathrm{DR}}} &= \frac{3\alpha^8}{V}\left(\frac{\Delta K}{K}\right)^2\frac{\omega^4}{v^3}\frac{\sin^4\left(\frac{\alpha|\mathbf{q}|\delta}{2}\right)}{\left(\frac{\alpha|\mathbf{q}|\delta}{2}\right)^4}\left(\frac{4\pi R^3}{3}\right)^2 \\ &\quad\times\left\{\frac{9[\cos(4|\mathbf{q}|R)-1+(4|\mathbf{q}|R)\sin(4|\mathbf{q}|R)]}{16^2(|\mathbf{q}|R)^6}\right. \\ &\quad\left.+\frac{9}{8(|\mathbf{q}|R)^4}\left[(|\mathbf{q}|R)^2-\frac{1}{4}\right]\right\}. \end{aligned} \tag{25}$$

3. Mass and force constant difference scattering

The combination of scattering due to differences in mass and force constant of a spherical nanoparticle in the Rayleigh regime is represented as the combination of Eqs. (18) and (25). This is similar to the additive nature of kinetic and potential energies in the Hamiltonian. The relaxation time is replaced by the scattering cross section using Eq. (4).

$$\begin{aligned} \frac{\sigma_{\mathrm{Rayleigh}}}{(\pi R^2)} &= \chi^4\cdot\left[\frac{\alpha^2}{4}\left(\frac{\Delta M}{M}\right)^2+3\alpha^8\left(\frac{\Delta K}{K}\right)^2\frac{\sin^4\left(\frac{\alpha|\mathbf{q}|\delta}{2}\right)}{\left(\frac{\alpha|\mathbf{q}|\delta}{2}\right)^4}\right] \\ &\quad\times\left\{\frac{\pi[\cos(4\chi)-1+(4\chi)\sin(4\chi)+32\chi^4-8\chi^2]}{16\chi^6}\right\}. \end{aligned} \tag{26}$$

The first parenthesis on the right-hand side of Eq. (26) represents the scattering strength. This term states that the more mass and/or force constant difference between the host medium and the spherical nanoparticle, the larger the scattering cross section. The last parenthesis represents functional dependence of the scattering cross section over the size parameter. When the size parameter reaches zero, i.e., the Rayleigh limit, the term in the second parenthesis goes to $16\pi/9$. Therefore, the scattering cross section in Eq. (26) is proportional to χ^4. The other limit where the size parameter reaches infinity, i.e., the geometrical scattering limit, the scattering cross section in Eq. (26) goes to χ^2. It is well known, how-

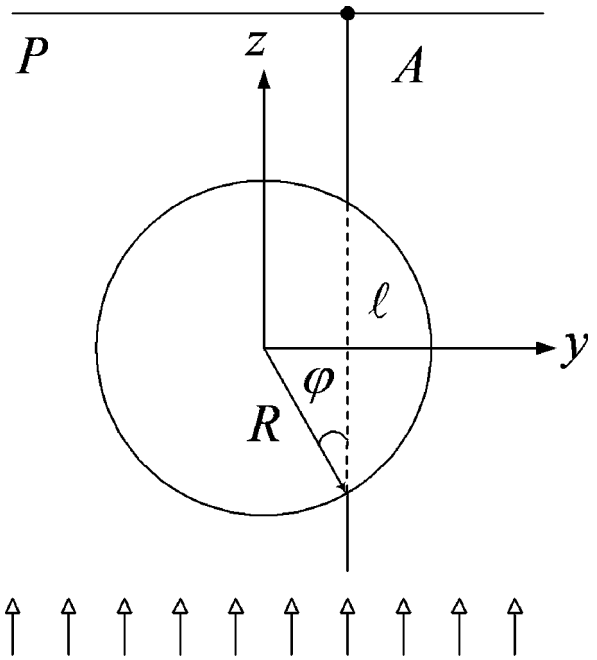

FIG. 2. Schematic diagram showing an incoming ray passing through the spherical nanoparticle. The length of the ray going through the spherical nanoparticle is ℓ. P is located at far downstream in z direction.

ever, that the scattering cross section near geometrical scattering regime is independent of the size parameter. This is believed to be a limitation of perturbation theory, i.e., it is valid only in one limit. To overcome this, we will now explore scattering in the geometrical scattering limit. This solution, however, will not be valid near in the Rayleigh regime. Hence, we will then bridge the two solutions in an approximate way such that the two limits are preserved.

B. Near geometrical scattering regime

The calculation of scattering cross section in the geometrical limit is based on the van de Hulst theorem.[2] Although it was developed to calculate electromagnetic wave scattering, we apply this theory in acoustic wave scattering. Before going into details of the calculation process, the basic assumptions of this method are discussed. Since this method is valid only when the size parameter is large, the scattering in this case is most likely in the forward direction. Also, when the acoustic impedance, Z, mismatch between the host medium and the spherical nanoparticle is not large, $Z'/Z \approx 1$, the backscattering can be neglected. Furthermore, the forward scattering tends to follow a straight path with small deflection. This approximation is generally acceptable for a solid-solid interface because the acoustic impedance mismatch between solids tends to be near unity. For electromagnetic wave scattering, crude assumptions such as that above lead to approximate solutions that are remarkably close to the Mie solution. It correctly explains the size parameter dependent peaks of the Mie solution, and with small improvements, errors compared with Mie solution can be reduced[12] below 5% at size parameter greater than 20.

Figure 2 is a schematic diagram showing an incoming ray passing through the spherical nanoparticle. ℓ is the length of the ray going through the nanoparticle, $\ell = 2R\cos\varphi$. The phase lag associated with this length measured at point A in Fig. 2 is

$$2R\cos\varphi q\left(\frac{q'}{q}-1\right)=2\chi\left(\frac{q'}{q}-1\right)\cos\varphi. \tag{27}$$

Just like in the Mie theory,[1,2] the incoming wave is a plane wave, e^{iqz}, and the scattered wave is a spherical wave, $[f(\xi)/r]\cdot e^{iqr}$, where f denotes scattering amplitude depending on directional angle, ξ. The amplitude of the incoming wave is set to unity. The wave outside the spherical nanoparticle is the superposition of the incoming and scattered waves. Thus, the waves in the forward direction can be written as follows:

$$\psi = e^{[iqz+2i\chi(q'/q-1)\cos\varphi]} = e^{iqz} + [e^{2i\chi(q'/q-1)\cos\varphi}-1]e^{iqz}. \tag{28}$$

This equation should be compared with

$$\psi = e^{iqz} + \frac{f(0)}{r}e^{iqr} \approx e^{iqz} + \frac{f(0)}{z}e^{iqz+iq[(x^2+y^2)/2z]}, \tag{29}$$

where $f(0)$ denotes forward scattering amplitude. The first term in Eq. (29) denotes the wave field outside the spherical nanoparticle. The second term approximates the first term through a Taylor series expansion assuming that a plane (P in Fig. 2) measures the wave field located far downstream in z direction.[21] However, Eq. (28) is not directly equal to Eq. (29) because $f(0)$ appearing in Eq. (29) is the forward scattering amplitude measured at plane P as shown in Fig. 2, which is far downstream in z direction. Therefore, to get $f(0)$ the following equation needs to be solved:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{f(0)}{z}e^{iqz+iq[(x^2+y^2)/2z]}dxdy = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}[e^{2i\chi(q'/q-1)\cos\varphi}-1]e^{iqz}dxdy. \tag{30}$$

The left-hand side of Eq. (30) is

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{iq(x^2+y^2)/2z}dxdy = \frac{2\pi i z}{q}. \tag{31}$$

According to the optical theorem,[21] the scattering cross section is related to the forward scattering amplitude as

$$\sigma = \frac{4\pi}{q}\,\mathrm{Im}\,f(0). \tag{32}$$

This relation states that by measuring the forward scattering amplitude far downstream, the scattering cross section is deduced and the imaginary part of the forward scattering amplitude is proportional to the scattering cross section. Therefore, in the Rayleigh scattering regime where the scattering tends to be isotropic, the forward scattering amplitude is small and so is the scattering cross section. In geometrical scattering regime, where scattering tends to go forward, forward scattering amplitude increases and so does scattering cross section. Therefore, the scattering cross section is written as

$$\sigma_{\text{near geometrical}} = 2\pi R^2 \left\{ 1 - \frac{\sin\left[2\chi\left(\frac{q'}{q}-1\right)\right]}{\chi\left(\frac{q'}{q}-1\right)} + \frac{\sin^2\left[\chi\left(\frac{q'}{q}-1\right)\right]}{\left[\chi\left(\frac{q'}{q}-1\right)\right]^2} \right\}, \tag{33}$$

where the ratio between the scattered and incoming wave vector is related to the mass and force constant as

$$\frac{q'}{q} - 1 = \frac{\sqrt{\frac{K}{M}}}{\sqrt{\frac{K+\Delta K}{M+\Delta M}}} - 1 = \frac{\sqrt{1+\frac{\Delta M}{M}}}{\sqrt{1+\frac{\Delta K}{K}}} - 1. \tag{34}$$

Equation (33) correctly captures the geometrical scattering limit, since, as the size parameter approaches infinity, the scattering cross section reaches twice the projected area of the spherical nanoparticle. Because of diffraction, scattering occurs near the edge of the nanoparticle, which enlarges the scattering cross section making it twice the geometrical projection area of the nanoparticle.[1]

C. Bridging between two extremes

As in Eq. (1), we proposed to connect two extremes, Eqs. (26) and (33), with the following simple relationship:

$$\frac{1}{\sigma_{\text{total}}} = \frac{1}{\sigma_{\text{Rayleigh}}} + \frac{1}{\sigma_{\text{near geometrical}}}. \tag{35}$$

The effects of size distributions of spherical nanoparticles are incorporated as a statistical distribution function. The gamma distribution,[22] which deals only with positive numbers, is chosen in this study, since the size of the spherical nanoparticle cannot be negative. Therefore, the scattering cross section in Eq. (35) is

$$\sigma_{\text{sct}} = \int_0^\infty \pi R^2 \left(\frac{\sigma_{\text{total}}}{\pi R^2}\right) \left[\frac{R^{A-1} e^{-R/B}}{B^A \Gamma(A)}\right] dR, \tag{36}$$

where A is the shape parameter, B is the scale parameter, and $\Gamma(A)$ is the gamma function. The mean of the distribution is equal to AB and the variance is equal to AB^2.

III. RESULTS AND DISCUSSIONS

The interesting aspects of scattering due to spherical nanoparticles can be deduced if we revisit how we derived Eqs. (26) and (33), and take a closer look at the terms in those equations. First, quantum-mechanical perturbation theory was used to derive Eq. (26). The perturbed Hamiltonian arises from changes in the mass and/or force constant. Therefore, we can deduce the fact that, in the Rayleigh scattering regime, both changes in the mass and/or force constant are important and they appear in Eq. (26). Second, the basic assumption made in deriving Eq. (33) is that the acoustic impedance mismatch between the host medium and the spherical nanoparticle is small. What has a greater effect on scattering cross section in the geometrical scattering regime is the path length, ℓ, and the associated phase lag. Thus, the size of the spherical nanoparticle is a more important factor in calculating scattering cross section near geometrical scattering regime.

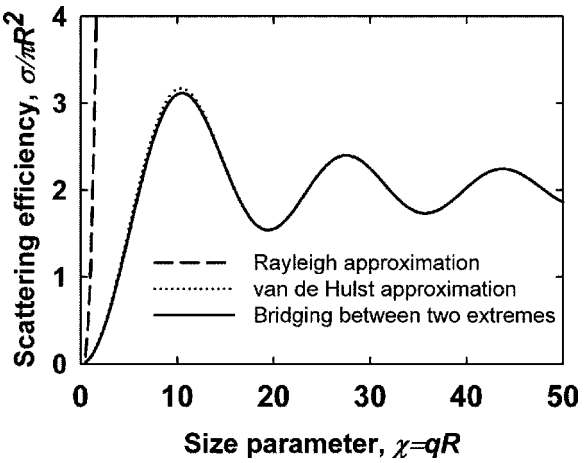

FIG. 3. Scattering efficiency vs size parameter of Rayleigh, near geometrical approximation and combinations of these two with Eq. (35). R is the radius of a spherical nanoparticle and q is the incoming wave vector.

Figure 3 shows the scattering efficiency defined as the scattering cross section divided by projection area of the spherical nanoparticle versus size parameter of Rayleigh, near geometrical approximation and combinations of these two with Eq. (35). The values that we used in the calculation are $\Delta M/M = 0.449$, and $\Delta K/K = 1.242$. This simulates the scattering cross section of ErAs nanoparticles epitaxially embedded in $In_{0.53}Ga_{0.47}As$.[23] The trigonometric ratio, α, is set to $1/\sqrt{2}$ for simplicity. We also set $q\delta$ to be much smaller than unity. The oscillation shown in the figure is due to interference effects as the near-geometrical approximation is based on anomalous diffraction. As shown in the figure, the Rayleigh approximation fails at large size parameter. Even though Eq. (35) is simple, it correctly connects two extremes.

Figure 4(a) shows the effect of polydispersion of spherical nanoparticles on scattering efficiency, which is scattering cross section divided by projected area based on the mean diameter of spherical nanoparticles. All three cases have the same mean diameter of spherical nanoparticles, but the standard deviation differs among them. Since the gamma distribution [see Fig. 4(b)] deals only with positive numbers, the standard deviation can have larger values than the mean diameter of spherical nanoparticles. By increasing the standard deviation by an order of magnitude, the oscillations in the scattering cross section damps out. This is evident when comparing a standard deviation of 0.06 to 0.6 nm. The oscillation is due to constructive and destructive interference effects. As the size distribution increases, these diffraction peaks fade away. As the standard deviation further increases, the scattering cross section based on mean diameter eventually increases. An approximate quantitative explanation is the following. If we consider a large size parameter, where the scattering efficiency approaches 2, Eq. (36) can be approximated as

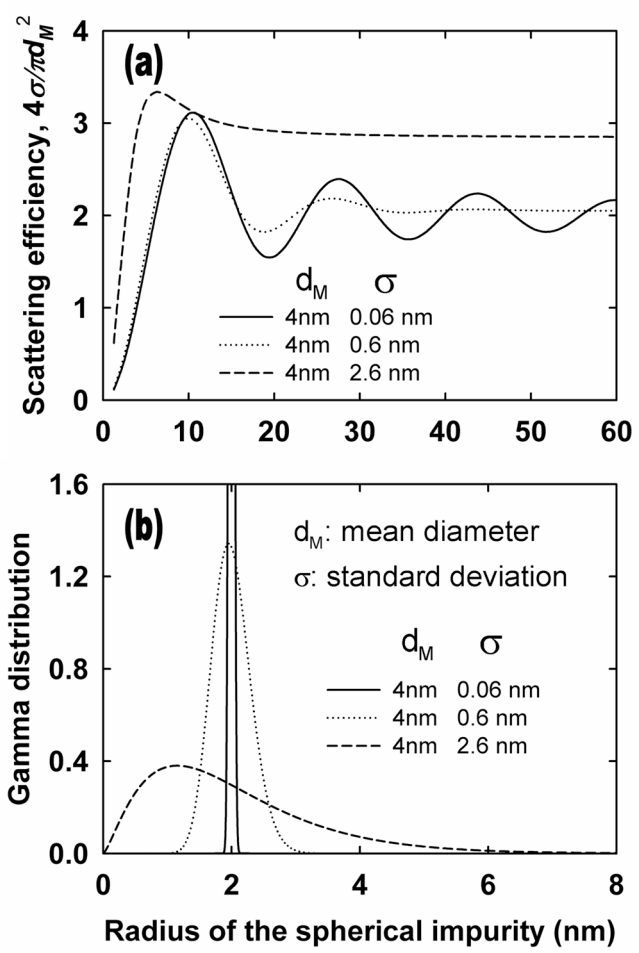

FIG. 4. (a) The effect of polydispersion of spherical nanoparticles on scattering efficiency vs size parameter. (b) Gamma distributions.

$$\sigma_{\mathrm{sct}} \approx \int_0^\infty R^2 \left[\frac{r^{A-1} e^{-R/B}}{B^A \Gamma(A)} \right] dR = \int_0^\infty R^2 g(R) dR, \qquad (37)$$

where $g(R)$ represents the gamma distribution function. The definition of variance, which is the square of the standard deviation, is

$$(\text{standard deviation})^2 = \text{var} = \int_0^\infty R^2 g(R) dR - \mu^2, \qquad (38)$$

where μ denotes the mean of radius of spherical nanoparticles and var donotes variance. Therefore, as the variance (or standard deviation) increases, the scattering cross section should increase, which can be inferred from Eqs. (37) and (38).

IV. CONCLUSIONS

In this paper, we proposed an approximate analytical solution to estimate the phonon scattering cross section, σ_{sct}, of polydispersed spherical nanoparticles as a function of χ, the size parameter. When $\chi \ll 1$, this is the so-called Rayleigh scattering regime. The other extreme, where $\chi \to \infty$, is the geometrical scattering regime. Analytical solutions for these two extremes were derived and bridged with a simple formula for the intermediate values of χ. The size distribution of nanoparticles was also considered by using a statistical distribution function. In the Rayleigh limit, what controls scattering cross section is how large are the changes in mass and/or force constant. In the near geometrical scattering regime, the path length, ℓ, through which the ray travels across the spherical nanoparticle and the associated phase lag are what determines the scattering cross section. In the case of polydispersion of spherical nanoparticles, as the size of nanoparticles deviates from its mean value, the oscillation term in the scattering cross section first dies out. As the deviation further increases, the scattering cross section based on mean diameter increases. Qualitatively, this indicates the large size distributions of spherical nanoparticle blocks ranges of phonon spectrum transport.

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