Light scattering in a non-equilibrium phonon gas

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Abstract. Light scattering spectrum from phonon-density fluctuations has been studied by extended thermodynamics of phonon gas. For hydrodynamic phonon regime, it has been found that the scattering spectrum essentially consists of two parts, one of which arises from equilibrated collective excitation of phonons, and the other of which arises from non-equilibrium, fast fluctuations due to collisions between individual phonons. At low temperature, where collisions between phonons are infrequent and local thermal equilibrium cannot be established within a length scale defined by the reciprocal of a scattering wave-vector, the spectrum cannot be separated into two components, and only one component due to unequilibrated fluctuations in phonon density persists. The theoretical spectral line shapes are in good agreement with the experimental light scattering spectra observed in many dielectric materials. Fits of the obtained expression to the experimental spectra that were observed in SrTiO$_3$ imply a possibility of second sound in this material.

1. Introduction

Recently, extended thermodynamics (ET) has succeeded in reproducing various non-equilibrium phenomena in physics including light scattering spectra [1, 2]. In the analyses of light scattering spectra, conventional macroscopic frameworks usually do for high density of scattering particles because local thermal equilibrium is well established within a length scale of $q^{-1}$, where $q$ is the scattering wave-vector defined as $q = 2k \sin(\theta/2)$ with $k$, the wave-vector of incident light, and $\theta$, the scattering angle. However, one often encounters violation of local thermal equilibrium for relatively low density of scattering particles. Even for such non-equilibrium regime, ET has been recognized to be valid [1, 2]. In this paper, we present an ET analysis for the light scattering spectra in dielectrics, or in a “phonon gas”. The spectral expression derived from the ET equations of Dreyer and Struchtrup [3] has been found to well reproduce and to be well fitted to the experimental spectra.

2. Theory

The ET-equation set of Dreyer and Struchtrup [3] is reproduced here:

$$\frac{\partial e^{(l)}(x, t)}{\partial t} + c^2 \frac{\partial p^{(l)}(x, t)}{\partial x} + \frac{1}{3} \frac{\partial e^{(l)}(x, t)}{\partial x} + \frac{\partial N^{(l)}(x, t)}{\partial x} = \frac{1}{\tau_R} p^{(l)} + b_{(l)} A c^{(l)} e^{(l)} - c^{(l)} e^{(l)}$$ (1)

$$\frac{\partial p^{(l)}(x, t)}{\partial t} = \frac{1}{\tau_N} \frac{\partial u^{(l)}(x, t)}{\partial x} - \frac{1}{\tau_R} p^{(l)} + b_{(l)} B c^{(l)} e^{(l)} - c^{(l)} e^{(l)}$$ (2)

$$\frac{\partial u^{(l)}_{<n>(x, t)}}{\partial t} + \alpha_n c^{(l)} \frac{\partial u^{(l)}_{<n-1>(x, t)}}{\partial x} + e_n c^{(l)} \frac{\partial u^{(l)}_{<n+1>(x, t)}}{\partial x} = - \left[ \frac{1}{\tau_N} + \frac{1}{\tau_R} \right] u^{(l)}_{<n>}(x, t)$$ (3)
Here, \( e^{(l)} \), \( p^{(l)} \), \( N^{(l)}_{<<c>}, \ldots \), and \( u^{(l)}_{<<c>}, \ldots \) are the energy density, the momentum density, the stress deviator (the deviatoric part of the stress tensor), \ldots , and the general flux deviator of order \( n = (1, 2, \ldots) \) for mode \( (l) \) or \( (t) \), longitudinal or transverse acoustic (LA or TA) mode, respectively. \( \alpha_n \) is defined as
\[
\alpha_n = \frac{\lambda}{2n(n-1)^2-1} \quad (n \geq 2).
\]
\( c^{(l)}_i \) is the (group) sound velocity. \( t^{(l)}_R \) and \( t^{(l)}_N \) are the relaxation times for resistive (momentum destroying) and normal (momentum conserving) processes of phonon-phonon scattering, respectively. \( A = (t^{(l)}_Rc^{(l)}_i + 2t^{(l)}_Rc^{(l)}_i)^{-1} + (t^{(l)}_Nc^{(l)}_i + 2t^{(l)}_Nc^{(l)}_i)^{-1} \) and \( B = (t^{(l)}_Nc^{(l)}_i + 2t^{(l)}_Nc^{(l)}_i)^{-1} \) are the coupling constants between the two phonon modes. Finally, the coefficients, \( b^{(l)}_n \), are given as \( b^{(l)}_0 = -2 \) and \( b^{(l)}_0 = +1 \). It is assumed that \( u_{<<c>_{max}+1>}_t = 0 \) for closure of the equation system [2], where \( n_{max} \) is the highest order of \( n \) considered.

The set of Eqs. (1) to (3) consists of \( 2n_{max} \) balance equations for the “fields” of the LA and the TA phonon gases. For example, Eq. (1) is the continuity equation for the energy density of the phonon gas of mode \( (l) \) with a production term due to the interaction with the other mode. It is known that the larger the number of the fields the higher degree of non-equilibrium the ET equation can be applied to because higher order fields, which are flux tensors of higher rank, contribute to faster fluctuations in the phonon gas. Thus, ET with infinite number of fields can account for ballistic propagation of phonons [1, 2]. Fourier-Laplace transform of Eqs. (1) to (3) yields a set of \( 2n_{max} \) equations with respect to \( q \) and \( s \), where \( s \) is the Laplace operator. The dynamic form factor for light scattering from phonon-density fluctuations is given, e.g., for the LA mode, as
\[
S_{LA}(q, s) \approx \frac{\langle e^{(l)}_y(q, 0)e^{(l)}_y(q, s) \rangle}{\langle e^{(l)}_x(q, 0)e^{(l)}_x(q, 0) \rangle} = \gamma^{(l)}_1 \times \frac{1 - 2B^2c^{(l)}_1c^{(l)}_0(s + Ac^{(l)}_3)\gamma^{(l)}_1\gamma^{(l)}_2}{1 - 2A^2c^{(l)}_0^2\gamma^{(l)}_1\gamma^{(l)}_2 - 2B\gamma^{(l)}_1\gamma^{(l)}_2\gamma^{(l)}_1\gamma^{(l)}_2W^{(l)}},
\]
where \( \gamma^{(l)}_1 \) are continued fractions that are recursively given as
\[
\gamma^{(l)}_1 = \left[ s + 1/\tau^{(l)} + \alpha \tau \right]^{-1} \quad (m \geq 3),
\]
with
\[
\gamma^{(l)}_2 = \left[ s + \alpha \tau \right]^{-1},
\]
\[
\gamma^{(l)}_3 = \left[ s + \frac{\alpha}{2} \frac{\tau}{\gamma^{(l)}_1} + \alpha \gamma^{(l)}_2 \right]^{-1},
\]
\[
\gamma^{(l)}_4 = \left[ s + \alpha \frac{\tau}{\gamma^{(l)}_1} + \alpha \gamma^{(l)}_2 \right]^{-1},
\]
where
\[
\alpha = 2, 1 \quad (l = l, t),
\]
\( \tau^{(l)} = \tau^{(l)}_N + 1/\tau^{(l)}_R \), \( W^{(l)} \) has been defined as
\[
W^{(l)} = c^{(l)}_0^2c^{(l)}_i \left[ B\left(s + Ac^{(l)}_3 - 2A^2c^{(l)}_0c^{(l)}_i\gamma^{(l)}_1\right) + A\gamma^{(l)}_2 \left( \frac{c^{(l)}_0}{c^{(l)}_i} + \frac{c^{(l)}_1}{c^{(l)}_i} \right) \right] + 2A^2Bc^{(l)}_0c^{(l)}_i\gamma^{(l)}_1\gamma^{(l)}_2\gamma^{(l)}_1\gamma^{(l)}_2.
\]
The spectrum for the TA mode, \( S_{TA}(q, s) \), is given simply by interchanging the superscripts \( (l) \) to \( (t) \) and vice versa. The total spectrum is a linear combination of \( S_{TA}(q, s) \) and \( S_{TA}(q, s) \), viz.,
\[
S_{ET}(q, \omega) = Re \left[ p^{(l)}S_{LA}(q, s) + p^{(l)}S_{TA}(q, s) \right]_{s = i\omega},
\]
where \( p^{(l)} \) and \( p^{(t)} \) are weighting coefficients. Terminating the continued fraction of Eq. (5) at a sufficiently deep level, e.g., \( m \geq 30 \) [2] with asymptotic expressions as
\[
\gamma^{(l)}_\infty = \frac{2}{c^{(l)}_0^2\omega^2} \left[ -(s + 1/\tau^{(l)}) + \sqrt{(s + 1/\tau^{(l)})^2 + c^{(l)}_1\omega^2} \right], \quad (l = l, t)
\]
enables effective inclusion of infinite number of higher order fluxes with relatively small number of field equations [1]. In our analysis, asymptotic termination was typically done at \( m = 30 \) in Eq. (5).

2.1. Hydrodynamic regime — thermal diffusion and second sound
If either normal or resistive phonon-collision is frequent enough in a length scale of \( q^{-1} \), the phonon gas can be treated as hydrodynamic. Then, Eq. (6) can be approximated as [4]
\[
S_{HD}(q, \omega) \approx P_1 \frac{2\omega q^2 \Gamma_{ss}}{(\omega^2 - \omega q^2)^2 + 4\omega^2 \Gamma_{ss}^2} + P_2 \frac{\Gamma_{c}}{\omega^2 + \Gamma_{c}^2} = P_1 S_1(q, \omega) + P_2 S_2(q, \omega),
\]
where
where we have defined $\Gamma_{ss}$ and $\Gamma_c$ respectively as

$$\Gamma_{ss} \equiv \frac{2}{15} \bar{c}^2 q^2 \tau_N + \frac{1}{2\tau_R}, \quad \Gamma_c \equiv \frac{1}{\tau_R} + \frac{1}{\tau_N} + 1.23 \bar{c} q.$$  

Here, we have assumed for simplicity an average sound velocity $\bar{c}$, and an average relaxation times $\tau_N$ and $\tau_R$ for LA and TA modes.

In Eq. (7), $S_1(q, \omega)$ comes from the equilibrated collective motion of a phonon gas, whose natural frequency has been defined as $\omega_0 \equiv \bar{c} q/\sqrt{\mathcal{D}}$. If $\Gamma_{ss} > \omega_0$, the phonon gas is overdamped, yielding a central Lorentzian due to thermal diffusion as

$$S_1(q, \omega) \approx \frac{\Gamma_D}{\omega^2 + \Gamma_D^2}, \quad \text{with} \quad \Gamma_D = D_{th} q^2,$$

where $D_{th} = \frac{1}{2} \bar{c}^2 \tau_R$ is the thermal diffusivity. If $\Gamma_{ss} < \omega_0$, the phonon gas becomes under-damped and exhibits a resonance at a frequency $\omega_{ss} = \sqrt{\omega_0^2 - \Gamma_{ss}^2}$, which is the frequency of “second-sound”, the density wave of phonons. Note that we are also assuming that $q \bar{c} \tau_N < 1$ in this case from the requirement of hydrodynamic regime. Thus, the total condition for the second sound observation is that

$$\Gamma_{ss} < \omega_0 < \tau_N^{-1}, \quad (8)$$

which corresponds to a frequency window for second sound to be observed for a given value of $q$. The spectrum for second sound is a “doublet” with frequency shifts at $\omega = \pm \omega_{ss}$.

$S_2(q, \omega)$ in Eq. (7) arises from kinetic collisions between individual phonons, which is a non-thermodynamic origin in contrast to the first term, $S_1(q, \omega)$. Therefore, the light scattering spectrum in a phonon gas in hydrodynamic regime consists of two parts, one of which is thermodynamic and the other of which is non-thermodynamic. In particular, if resistive scattering is dominant as in many dielectrics at high temperatures, the spectrum becomes a sum of two unshifted Lorentzians, which have been actually observed in many dielectrics [5, 6]. However, the origin of this broader central peak, $S_2(q, \omega)$, remained open for three decades. The broader central peak supersedes the second-sound doublet onto itself if the window condition Eq. (8) is satisfied.

2.2. Ballistic regime

If $q \bar{c} \tau_R, q \bar{c} \tau_N \gg 1$, Eq. (6) reduces to virtually one quasielastic component, and can be approximated as

$$S_{bb}(q, \omega) \propto \tan^{-1} \tau(\omega + \bar{c} q) - \tan^{-1} \tau(\omega - \bar{c} q), \quad (9)$$

which is consistent with what has been obtained in two-phonon difference light scattering (TPDS) on a single phonon branch [7, 8]. Since the TPDS model may be defined only in the ballistic phonon regime, we see that ET can indeed bridge the hydrodynamic and ballistic regimes.

If $\tau_N$ is much shorter than $\tau_R$, the second-sound resonance affects the spectral shape and Eq. (9) is not a good approximation. In that case, although second sound cannot be defined within $q^{-1}$, it can be shown [4] that an unequilibrated collective propagation of phonons can still give rise to a broad non-Lorentzian doublet in the spectrum.

3. Discussion

We have fitted Eq. (6) to the experimental spectrum reported in SrTiO$_3$ [9, 6], which is well known as a “quantum paraelectric” [9]. Figure 1 shows the temperature dependence of the observed [6] and fitted spectra from 6.4 K to 295 K. The “double Lorentzian” structure at high $T$ and the “doublet on broad central peak” at low $T$ have been well reproduced by the present model. The parameters obtained in the fit have been found to be quite reasonable for this material [4], e.g., $\tau_R = 10$ ps, $\tau_N = 3.3$ ps,
Figure 1. The light scattering spectra observed in SrTiO$_3$ [6] and fits of ET function (Eq. (6)). The “LA” and “TA” represent the Brillouin scattering lines corresponding to the longitudinal acoustic and the transverse acoustic modes, respectively. Constant backgrounds were added in the fits except for 6.4K and 15K, for which appropriate background structures were added.

and \( \bar{c} = 4800 \text{ m/s} \) at 30K. These values and \( q = 6.0 \times 10^7 \text{ m}^{-1} \) do satisfy the window condition for second sound (Eq. (8)). This implies that the observed doublet might be ascribed to second sound as predicted theoretically [10] and as proposed by Hehlen et al [9]. However, at lower temperatures, e.g., at 6.4K, \( q \bar{c} \tau_N \) was found to be as large as 3, which indicate a non-equilibrium (non-hydrodynamic) regime. The doublet spectrum at this temperature then should not be attributed to second sound in its classical meaning for the employed value of \( q \). In this case, it might be more suitable to state that the doublet is arising from unequilibrated collective propagations of phonons [4].

4. Summary
We derived ET spectral function for a mixture of LA and TA phonon gases from the ET-equation set of Dreyer and Struchtrup [3]. We found that the spectra observed in SrTiO$_3$ could be well fitted in a unified manner with our ET spectral function in a wide range of temperature covering from hydrodynamic to non-hydrodynamic regimes. The result for SrTiO$_3$ indicated that the controversial origin for the extra Brillouin spectrum at around 30K might be second sound as was originally proposed by Hehlen et al [9].

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