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Semi‒analytic theory of multiphonon effects on the static structure factors of warm solids

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Synopsis Analysis of density fluctuations in condensed matter through the static structure factors is a fundamental issue in statistical mechanics relevant to a characterization of disorder and uniformity. A new semi-analytic formula is proposed for the static structure factor of solids at finite temperatures by taking into account multiphonon diffuse scattering up to infinite order. The formula is applicable to the entire wavenumber range and computationally more efficient than other theoretical models.

Abstract A semi-analytic formula for the temperature-dependent static structure factor $S(k)$ of polycrystalline and amorphous solids applicable to the entire wavenumber (k) range is derived. The formula describes thermal diffuse scattering due to multiphonon processes entirely by a single kernel function without resorting to the standard peruturbation expansion. It is analytically proven that $S(k \to 0)$ is determined from the one-phonon term, whereas the asymptotic limit $S(k \to \infty) = 1$ can be reproduced through a Gaussian integral of the multiphonon term. The formula also reveals that an enhancement of the one-phonon scattering intensity at each Bragg point is expressed as a logarithmic singularity. Numerical examples for a face-centred-cubic polycrystal near the melting point are shown. The present formula is computationally more efficient than other theoretical models, requiring only a one-dimensional integration to obtain $S(k)$ once the elastic part of the structure factor and the Debye-Waller factor are given.

Keywords: static structure factor; thermal diffuse scattering; multiphonon processes.

1. Introduction

The static structure factor, representing the spectrum of density fluctuations in wavevector space, plays an essential role in characterising the microscopic structures of various types of materials such as solids (Toby & Egami, 1992), liquids (March & Tosi, 1991), plasmas (Ichimaru, 1992), and nano-

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structured materials (Billinge, 2019). In x-ray or neutron diffraction experiments for crystals (Wallen, 1990; Nield & Keen, 2001), the measured structure factor typically consists of an elastic scattering part indicating a series of sharp Bragg peaks and an inelastic scattering part stemming from phonons; the latter is observed as thermal diffuse scattering (TDS). Though TDS intensities are generally weaker than the Bragg peaks, it has been pointed out that the TDS component of the structure factors at finite temperatures may crucially affect the transport coefficients such as the electrical conductivity near the melting point (Baiko *et al*., 1998). Analysis of density fluctuations in condensed matter through the structure factors is a fundamental issue in statistical mechanics relevant to a characterization of disorder and uniformity (Torquato, 2018).

The standard theory of TDS, based on the harmonic approximation of lattice vibrations, adopts the Taylor expansion of the scattering intensity into one-phonon, two-phonon, and higher-order processes (Maradudin *et al*., 1971; Wallen, 1990). The one-phonon scattering is usually dominant, and hence higher-order effects may be either neglected or evaluated approximately in terms of lower-order terms (Meisel & Cote, 1977; Wallen, 1990). Such approximate formulae cannot elucidate the overall behaviours of the structure factors from small to large wavenumbers. A formal expression for all-phonon scattering intensity is available and applicable to first-principles analysis of TDS patterns in real materials (Zacharias *et al*., 2021), whereas analytic studies on the properties of multiphonon TDS structure factors from general viewpoint have rarely been reported.

In this paper, we present a semi-analytic formula for the static structure factor of polycrystalline and amorphous solids at finite temperatures, where multiphonon scattering is taken into account to all orders through an integral kernel function without employing the standard Taylor expansion. The formula properly reproduces the asymptotic limits at both small and large wavenumbers, ensuring a wide range of applicability. The present formula is expressed as a compact one-dimensional integral of the elastic part of the structure factor and the Debye-Waller factor; it is numerically more efficient than currently existing models that require two-dimensional integrals.

2. Theoretical formulation

2.1. General background

The static structure factor $S(\boldsymbol{k})$ of a system consisting of N identical atoms may generally be defined as $S(\boldsymbol{k}) = (1/N)\langle \rho_{\boldsymbol{k}}(0)\rho_{-\boldsymbol{k}}(0)\rangle$, where $\rho_{\boldsymbol{k}}(t) = \sum_{n=1}^{N} \exp[-i\boldsymbol{k}\cdot\boldsymbol{r}_n(t)]$ is the Fourier transform of the density operator, $\boldsymbol{r}_n(t)$ is the position of the nth atom at time t, and the angular brackets stand for a statistical average (Torquato, 2018). For solids, we may write as $\boldsymbol{r}_n(t) = \boldsymbol{r}_n + \boldsymbol{u}_n(t)$, where $\boldsymbol{r}_n \equiv \langle \boldsymbol{r}_n(t)\rangle$ is an average atomic position and $\boldsymbol{u}_n(t)$ is a displacement therefrom. The density operator is likewise decomposed as $\rho_{\boldsymbol{k}}(t) = \langle \rho_{\boldsymbol{k}}\rangle + \delta\rho_{\boldsymbol{k}}(t)$. In the harmonic theory of lattice vibrations

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(Maradudin *et al.* 1971), the average part can be calculated as $\langle\rho_{\boldsymbol{k}}\rangle \equiv \langle\rho_{\boldsymbol{k}}(t)\rangle = e^{-W(\boldsymbol{k})}\sum_{n=1}^{N} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_n}$, where

$$W(\boldsymbol{k}) = \frac{1}{2NM}\sum_{\boldsymbol{q}s}^{\mathrm{BZ}} \frac{\hbar|\boldsymbol{k}\cdot\boldsymbol{e}(\boldsymbol{q}s)|^2}{2\omega_s(\boldsymbol{q})}\coth\left[\frac{\hbar\omega_s(\boldsymbol{q})}{2k_BT}\right] \tag{1}$$

is the exponent of the Debye-Waller factor. Here, k_{B} is the Boltzmann constant, T is the temperature, M is the atomic mass, $\omega_s(\boldsymbol{q})$ is the frequency of a phonon of mode s, wavevector $\mathbf{q}$, and polarization $\boldsymbol{e}(\boldsymbol{q}s)$ in the first Brillouin zone (BZ). The static structure factor can thus be expressed as

$$S(\boldsymbol{k}) = \frac{1}{N}[\langle\rho_{\boldsymbol{k}}\rangle\langle\rho_{-\boldsymbol{k}}\rangle + \langle\delta\rho_{\boldsymbol{k}}(0)\delta\rho_{-\boldsymbol{k}}(0)\rangle] = e^{-2W(\boldsymbol{k})}S_{\mathrm{el}}(\boldsymbol{k}) + S_{\mathrm{TDS}}(\boldsymbol{k}), \tag{2}$$

where

$$S_{\mathrm{el}}(\boldsymbol{k}) = \frac{1}{N}\sum_{m,n=1}^{N} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_m-\boldsymbol{r}_n)} \tag{3}$$

is the elastic part, and

$$S_{\mathrm{TDS}}(\boldsymbol{k}) = \frac{e^{-2W(\boldsymbol{k})}}{N}\sum_{m,n=1}^{N} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_m-\boldsymbol{r}_n)}\left[e^{w(\boldsymbol{k},\boldsymbol{r}_m-\boldsymbol{r}_n)} - 1\right] \tag{4}$$

represents the TDS part (Maradudin *et al.* 1971), with

$$w(\boldsymbol{k},\boldsymbol{r}) \equiv \frac{1}{NM}\sum_{\boldsymbol{q}s}^{\mathrm{BZ}} \frac{\hbar|\boldsymbol{k}\cdot\boldsymbol{e}(\boldsymbol{q}s)|^2}{2\omega_s(\boldsymbol{q})}\coth\left[\frac{\hbar\omega_s(\boldsymbol{q})}{2k_BT}\right]\cos(\boldsymbol{q}\cdot\boldsymbol{r}). \tag{5}$$

Equations (1)-(5) provide the basis for first-principles analyses of phonon effects on the structure factor (Zacharias *et al.*, 2021).

Through comparison of Eqs. (1) and (5) one finds a general relation $w(\boldsymbol{k},0) = 2W(\boldsymbol{k})$ for $\boldsymbol{r} = 0$. Analytic calculations of (5) for nonzero $\mathbf{r}$ can be performed by adopting the Debye approximation (Maradudin *et al.* 1971) and assuming isotropic phonon dispersion, $\omega_s(\boldsymbol{q}) = \bar{c}q$ for all s (=1, 2, 3) and $q \equiv |\boldsymbol{q}| \leq q_{\mathrm{D}}$. Here, $\bar{c}$ is the average sound speed, $q_{\mathrm{D}} \equiv (6\pi^2 n)^{1/3}$ is the Debye cutoff wavenumber, and n is the number density of atoms. We also adopt a high-temperature approximation $T \gg T_{\mathrm{D}}$, with $T_{\mathrm{D}} \equiv \hbar\bar{c}q/k_{\mathrm{B}}$ denoting the Debye temperature, which may be justified near the melting point. Equation (5) then reduces to (Wallen, 1990)

$$w(k,r) = 2W(k)\frac{\mathrm{Si}(q_{\mathrm{D}}r)}{q_{\mathrm{D}}r}, \tag{6}$$

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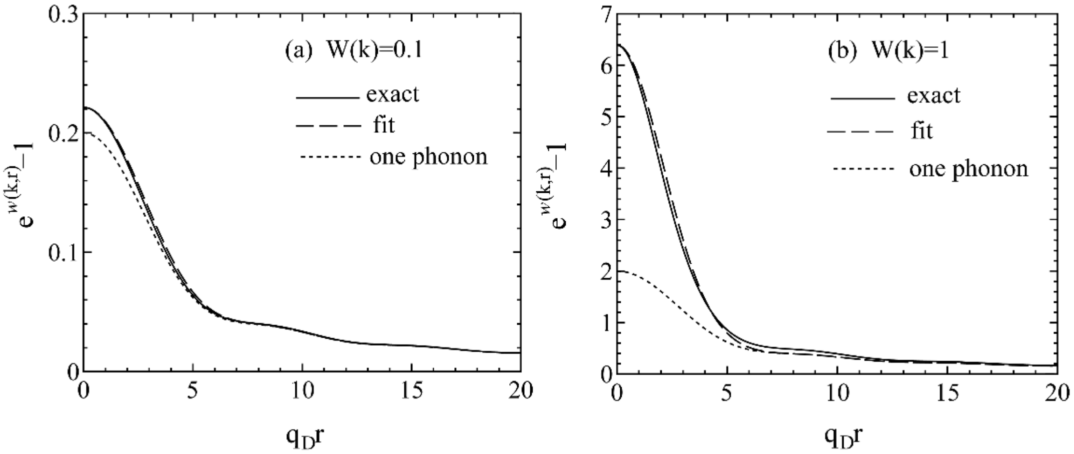

Figure 1 Plots of the function $e^{w(k,r)}-1$ for (a) $W(k)=0.1$ and (b) $W(k)=1$. Solid curve is the exact result; dashed curve is based on fitting formula (9); dotted curve is the one-phonon contribution $w(k,r)$ given by (6).

where $\mathrm{Si}(x) \equiv \int_0^x dt \frac{\sin t}{t}$ stands for the sine integral. The Debye-Waller exponent (1) is likewise calculated as

$$W(k) = \frac{3k^2}{2q_D{}^2} T_*, \tag{7}$$

where $T_* \equiv k_B T / M\bar{c}^2$ is a dimensionless temperature. Note that Eq. (6) depends only on the magnitudes $k \equiv |\boldsymbol{k}|$ and $r \equiv |\boldsymbol{r}|$.

2.2. Integral formula

When evaluating Eq. (4), one often employs a Taylor expansion $e^{w(k,r)}-1 = w(k,r) + w^2(k,r)/2! + \cdots$, where the right-hand side represents one-phonon, two-phonon, and higher-order processes. Here, we avoid such an expansion and treat $e^{w(k,r)}-1$ as a single function. In accordance with (6), we notice the limiting behaviours in r-space,

$$e^{w(k,r)}-1 \approx \begin{cases} \exp\left\{2W(k)\left[1-\frac{(q_D r)^2}{18}\right]\right\}-1, & \text{for } q_D r \ll 1, \\ 2W(k)\frac{\mathrm{Si}(q_D r)}{q_D r}, & \text{for } q_D r \gg 1. \end{cases} \tag{8}$$

We propose an approximate interpolation formula connecting these two limits as

$$e^{w(k,r)}-1 \simeq 2W(k)\frac{\mathrm{Si}(q_D r)}{q_D r} + \left[e^{2W(k)} - 2W(k) - 1\right] e^{-B(k)(q_D r)^2}, \tag{9}$$

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$$B(k) \equiv \frac{W(k)}{9[1-e^{-2W(k)}]}. \tag{10}$$

We remark that the k-dependence enters (9) and (10) only through the Debye-Waller exponent $W(k)$. The plot of $e^{w(k,r)}-1$ in r-space is illustrated in Figure 1. For $q_{\mathrm{D}}r \gg 1$, it is dominated by the one-phonon term and proportional to $1/r$; such a long-range tail results from the linear phonon dispersion assumed in the Debye model. The remaining contribution from the multiphonon term increases significantly as $q_{\mathrm{D}}r$ decreases, especially when k is large. Accuracy of fitting formula (9) is clearly indicated over a wide range of k and r.

The Gaussian expression in (9) has an advantage such that its Fourier transform, $y(k,\boldsymbol{q}) \equiv ne^{-2W(k)}\int d\boldsymbol{r}[e^{w(k,r)}-1]e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}$, can be calculated analytically (Gradshteyn & Ryzhik, 2000). The result depends only on $q=|\boldsymbol{q}|$ and consists of two terms, $y(k,q)=y_1(k,q)+y_{\mathrm{m}}(k,q)$, where

$$y_1(k,q) = \frac{2}{3}W(k)e^{-2W(k)}\frac{q_{\mathrm{D}}^2}{q^2}\Theta(q_{\mathrm{D}}-q) \tag{11}$$

is the one-phonon scattering term with

$$\Theta(q_{\mathrm{D}}-q) \equiv \begin{cases} 1, \text{ for } q<q_{\mathrm{D}} \\ 1/2, \text{ for } q=q_{\mathrm{D}} \\ 0, \text{ for } q>q_{\mathrm{D}} \end{cases}$$

denoting the Heaviside step function. The multiphonon term can be written as

$$y_{\mathrm{m}}(k,q) = \frac{1-e^{-2W(k)}[1+2W(k)]}{6\pi^{1/2}B(k)^{3/2}}\exp\left[-\frac{1}{4B(k)}\frac{q^2}{q_{\mathrm{D}}^2}\right]. \tag{12}$$

By substituting the inverse Fourier transform $e^{w(k,r)}-1=(e^{2W(k)}/N)\sum_{\boldsymbol{q}}y(k,q)\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ back into Eq. (4) and using Eq. (3), we obtain

$$S_{\mathrm{TDS}}(\boldsymbol{k}) = \frac{1}{N}\sum_{\boldsymbol{q}}y(k,|\boldsymbol{k}-\boldsymbol{q}|)\,S_{\mathrm{el}}(\boldsymbol{q}). \tag{13}$$

We shall mainly focus on isotropic samples such as powder crystals and amorphous solids, and hence take an angular average of Eq. (13). We define $\bar{y}(k,q)$ as an average of $y(k,|\boldsymbol{k}-\boldsymbol{q}|)$ over the directions of **k**, which can be calculated according to $\bar{y}(k,q)\equiv(1/2kq)\int_{|k-q|}^{k+q}ds\,sy(k,s)$; this integration can be carried out analytically again, leading to

$$\bar{y}(k,q)=\bar{y}_1(k,q)+\bar{y}_{\mathrm{m}}(k,q). \tag{14}$$

Here, the one-phonon term can be calculated as

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$$\bar{y}_1(k,q) = \frac{W(k)e^{-2W(k)}}{3}\frac{q_{\mathrm{D}}^2}{kq}\mathscr{F}(k,q), \tag{15}$$

$$\mathscr{F}(k,q) \equiv \begin{cases} 0 & \text{for } q_{\mathrm{D}} \le |k-q|, \\ \ln\dfrac{q_{\mathrm{D}}}{|k-q|} & \text{for } |k-q| < q_{\mathrm{D}} \le k+q, \\ \ln\dfrac{k+q}{|k-q|} & \text{for } k+q < q_{\mathrm{D}}. \end{cases} \tag{16}$$

The multiphonon term is likewise obtained as

$$\bar{y}_{\mathrm{m}}(k,q) = \frac{1-e^{-2W(k)}[1+2W(k)]}{6[\pi B(k)]^{1/2}}\frac{q_{\mathrm{D}}^2}{kq}$$
$$\times\left\{\exp\left[-\frac{1}{4B(k)}\frac{|k-q|^2}{q_{\mathrm{D}}^2}\right]-\exp\left[-\frac{1}{4B(k)}\frac{(k+q)^2}{q_{\mathrm{D}}^2}\right]\right\}. \tag{17}$$

When the elastic structure factor for an infinite crystal $S_{\mathrm{el}}(\boldsymbol{q}) = N\sum_{\boldsymbol{G}}\delta_{\boldsymbol{q},\boldsymbol{G}}$ is adopted, where **G** represents the reciprocal lattice vector, Eq. (13) leads to a discrete sum, $S_{\mathrm{TDS}}(k) = \sum_{\boldsymbol{G}}\bar{y}(k,|\boldsymbol{G}|)$. For polycrystals or amorphous solids, $S_{\mathrm{el}}(\boldsymbol{q})$ is a continuous function of q and hence Eq. (13) can be rewritten as

$$S_{\mathrm{TDS}}(k) = \bar{y}(k,0) + \frac{1}{2\pi^2 n}\int_0^\infty dq\, q^2\bar{y}(k,q)S_{\mathrm{el}}(q). \tag{18}$$

We remark here that $\boldsymbol{q} = 0$ is a singular point of $S_{\mathrm{el}}(\boldsymbol{q})$ so that the contribution from $S_{\mathrm{el}}(0)(=N)$ has been separated out in the first term on the right-hand side of (18); it is convenient to evaluate this term by using the relation $\bar{y}(k,0) = y(k,k) = y_1(k,k) + y_{\mathrm{m}}(k,k)$ in conjunction with Eqs. (11) and (12). Equation (18) takes the form of a one-dimensional integral formula, where $\bar{y}(k,q)$ plays the role of a kernel function. Analytic properties of the kernel function will be discussed in the next section.

3. Results

3.1. Analytic properties

3.1.1. Small-wavenumber limit

In the $k \to 0$ limit, we have $e^{-2W(k)} \to 1$ and $B(k) \to 1/18$; only the $q = 0$ component of the one-phonon term (15) contributes to (18). Because $\mathscr{F}(k, q \to 0) = 2q/k$ for fixed k in (16), it follows that

$$S_{\mathrm{TDS}}(k \to 0) = \lim_{k\to 0}\bar{y}_1(k,0) = \lim_{k\to 0}\frac{2W(k)}{3}\frac{q_D^2}{k^2} = T_*. \tag{19}$$

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We note that the q-integral on the right-hand side of (18) vanishes as $k \to 0$ since $\mathscr{F}(k \to 0, q) = 2k/q$ for finite q ($< q_{\mathrm{D}}$). For the case $S_{\mathrm{el}}(k \to 0) = 0$ as in crystals, we have $S(k \to 0) = T_* = k_B T / M\bar{c}^2$, in agreement with the expression by Kim & Torquato (2018) obtained for a simple cubic lattice with nearest-neighbour harmonic interaction. When the full structure factor $S(\boldsymbol{k})$ in three-dimensional **k**-space is concerned, only the longitudinal phonon whose polarization vector is parallel to **k** has to be retained; Kim & Torquato (2018) and Faber (1972) thus derived an expression $S(\boldsymbol{k} \to 0) = k_B T / M c_{\parallel}^2$ with $c_{\parallel}$ denoting the longitudinal sound velocity. Analogous relation $S(k \to 0) = k_B T / M c_T^2$ was obtained for liquids by hydrodynamic theory (March & Tosi, 1991), where c_T stands for the isothermal sound velocity. In thermal equilibrium, this equation reduces to the compressibility relation $S(k \to 0) = n k_B T \chi_T$ (March & Tosi, 1991), where χ_T is the isothermal compressibility which is related to c_T via $1/\chi_T = n M c_T^2$. Faber (1972) argued, however, that these equations for solid and liquid phases are not completely equivalent, since the difference between isothermal and adiabatic sound velocities is obscure within the harmonic theory of solids.

A rough estimation of $S(k \to 0)$ at the melting point may be made through calculations of T_* by the Lindemann's criterion for the mean square displacement of lattice vibrations (Maradudin *et al.*, 1971). According to the compilation by Lawson (2009), we may evaluate approximately as $S(k \to 0) = T_* \approx 0.0042$ - 0.037 for monatomic elements with cubic lattice structures. These values are comparable to the observed values of $S(0)$ for simple liquids at the melting point, as listed in Table 2.7 of Faber (1972). In amorphous solids and glasses, which may be out of equilibrium, both $S_{\mathrm{el}}(k \to 0)$ and $S_{\mathrm{TDS}}(k \to 0)$ may contribute to $S(k \to 0)$. The values of $S(k \to 0)$ for amorphous silicon and vitreous silica computed by de Graff and Thorpe (2010) amount to about 0.04 and 0.1, respectively, which turn out to be larger than the values mentioned above for crystals; they ignored the phonon contribution $S_{\mathrm{TDS}}(k)$, however, by postulating that $S_{\mathrm{TDS}}(k) \propto k^2 \to 0$ for small k, contrary to our prediction (19).

3.1.2. Large-wavenumber limit

In the $k \to \infty$ limit, the one-phonon term (15) vanishes since $e^{-2W(k)} \to 0$ and hence we focus on the multiphonon term (17). Since $B(k) \to W(k)/9$, one finds

$$S_{\mathrm{TDS}}(k \to \infty) = \lim_{k \to \infty} \sqrt{\frac{3}{2\pi T_*}} \frac{1}{k^2} \int_0^\infty dq\, q \exp\left[-\frac{3|q-k|^2}{2T_* k^2} \right] S_{\mathrm{el}}(q). \tag{20}$$

The integrand on the right-hand side contains a Gaussian centred at $q = k$ with the full width of half maximum $\Delta \approx \sqrt{T_*} k$, multiplied by $S_{\mathrm{el}}(q)$; the latter may be evaluated with, e.g., the Debye scattering equation (Gelicio & Scardi, 2016),

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$$S_{\mathrm{el}}(q) = 1 + \frac{1}{N}\sum_{m\neq n}^{N} \frac{\sin(q|\boldsymbol{r}_m - \boldsymbol{r}_n|)}{q|\boldsymbol{r}_m - \boldsymbol{r}_n|}. \tag{21}$$

When k is large, the second term on the right-hand side of (21) oscillates rapidly within the Gaussian window $k - \Delta < q < k + \Delta$ and its average value is small; its contribution to $S_{\mathrm{TDS}}(k \to \infty)$ vanishes due to the additional decaying factor $1/k^2$ in (20). Consequently, we can set $S_{\mathrm{el}}(q) = 1$ in (20); the resultant q-integral can be performed analytically for large k as

$$\int_0^\infty dq\, q \exp\left[-\frac{3|q-k|^2}{2T_* k^2}\right] \approx k \int_{-\infty}^{\infty} dq \exp\left[-\frac{3|q-k|^2}{2T_* k^2}\right] = k^2\sqrt{\frac{2\pi T_*}{3}}, \tag{22}$$

yielding

$$S_{\mathrm{TDS}}(k \to \infty) = 1. \tag{23}$$

Since the first term on the right-hand side of Eq. (2) vanishes as $e^{-2W(k)} \to 0$, the total structure factor satisfies $S(k \to \infty) = 1$, as it should be; this conclusion can be inferred directly from the random nature of the atomic displacements $\boldsymbol{u}_n(t)$ obeying the Gaussian distributions (Maradudin *et al.* 1971).

A slightly different proof may be required for a single crystal whose elastic structure factor does not converge to unity but exhibits an infinite series of discrete Bragg peaks. In this case, we use the formula $S_{\mathrm{TDS}}(k) = \sum_{\boldsymbol{G}} \bar{y}(k, G)$ $(G \equiv |\boldsymbol{G}|)$ to obtain

$$S_{\mathrm{TDS}}(k \to \infty) = \lim_{k\to\infty} \sum_{\boldsymbol{G}\neq 0} \frac{1}{\sqrt{6\pi T_*}} \frac{q_D^3}{k^2 G} \exp\left[-\frac{3|G-k|^2}{2T_* k^2}\right].$$

When k is large, there are many reciprocal lattice points **G** contained within the Gaussian window $k - \Delta < G < k + \Delta$ and hence the summation over discrete **G** may be replaced by an integral,

$$\sum_{\boldsymbol{G}\neq 0} \frac{1}{G}\exp[\cdots] = \frac{1}{2\pi^2 n}\int_0^\infty dG\, G \exp[\cdots].$$

The resultant Gaussian integral is identical to (22) and we again arrive at (23).

3.1.3. One-phonon scattering

In intermediate-k regime, the factor $ln(q_{\mathrm{D}}/|k-q|)$ in the one-phonon scattering term (16) indicates a logarithmic singularity at $k = q$, which originates from the linear phonon dispersion in the Debye model. In crystals, as $S_{\mathrm{el}}(q)$ exhibits Bragg peaks at $q = G$, a logarithmic divergence of $S_{\mathrm{TDS}}(k)$ is predicted at $k = G$. Intuitive discussions on the appearance of such one-phonon peaks in the Debye model can be found in textbooks such as Fig. 2.7 of Faber (1972) and Fig. 3.6 of Nield & Keen (2001); numerical demonstrations have also been indicated in Fig. 11.17 of Warren (1990) and the

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paper of Wu, Houska & Rao (1994). To the author's knowledge, however, explicit analytic expressions as revealed by (16) have not been reported in the literature.

3.2. Numerical examples

We apply formula (18) to an ideally random face-centred-cubic (fcc) polycrystal near the melting point. The elastic structure factor $S_{\mathrm{el}}(k)$ has been computed with the Debye scattering equation (21) for a $15a \times 15a \times 15a$ fcc crystallite ($N = 14896$ atoms) with a denoting the side of the conventional fcc unit cell. The result is shown in Fig. 2. A large peak of $S_{\mathrm{el}}(k)$ for $ka < 4$ shown by the dotted line, which is due to a finite-size shape effect, has been eliminated in the following analysis.

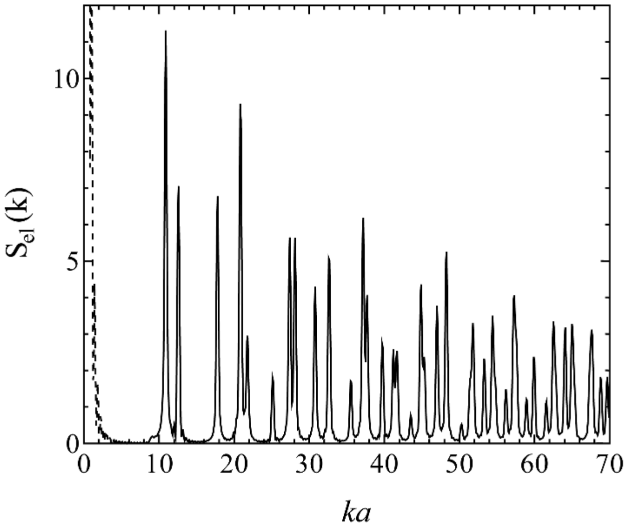

Figure 2 Elastic structure factor of an fcc crystallite ($N = 14896$) calculated by (21).

Figure 3 illustrates the plot of $S_{\mathrm{TDS}}(k)$ for $T_* = 0.01$ and 0.025 obtained from (18) by using the numerical data of $S_{\mathrm{el}}(k)$ shown in Fig. 2. Peaks of one-phonon scattering can be seen at reciprocal lattice points $\boldsymbol{G}_{hkl} = (2\pi/a)(h,k,l)$ where h, k, and l are all even or all odd. The first peak is located at $k = G_{111} = 2\sqrt{3}\pi/a$. It can be observed that $S_{\mathrm{TDS}}(k)$ is virtually constant $(= T_*)$ in the region $k < G_{111} - q_{\mathrm{D}}$ (i.e., $ka < 4.70$), and then it increases toward the first peak at $k = G_{111}$; this trend agrees qualitatively with Fig. 2.7 of Faber (1972). A small discontinuity at $k = q_{\mathrm{D}}$ ($ka = 6.19$), stemming from the step function in (11), can be regarded as an artefact of the Debye model due to a sudden cutoff of the phonon dispersion at $q = q_{\mathrm{D}}$. The one-phonon peaks appear successively at higher **G**-vectors, as already illustrated in the literature (Warren, 1990; Wu & Houska, 1994). As k increases, the one-phonon contribution (15) is suppressed by the Debye-Waller factor and the multiphonon term (17) prevails; $S_{\mathrm{TDS}}(k)$ eventually converges to unity, corroborating the asymptotic

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property (23). The convergence becomes faster as the temperature increases, manifesting a thermal enhancement of multiphonon effects.

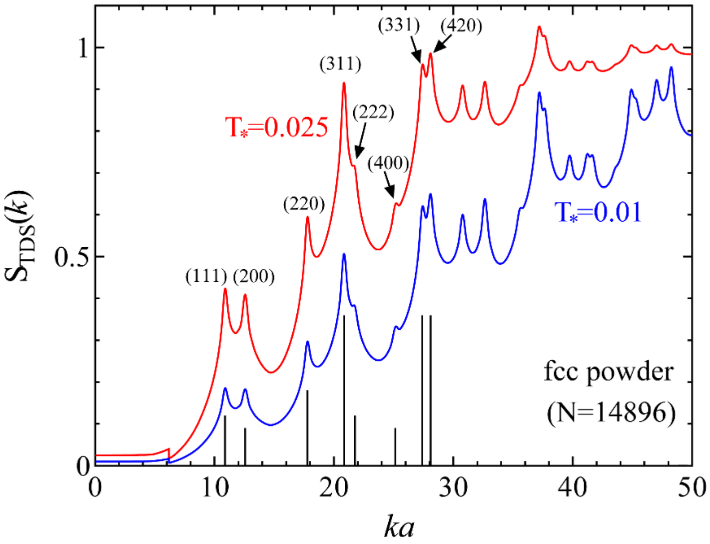

Figure 3 The TDS structure factor based on Eq. (18) for an fcc polycrystal at $T_* = 0.01$ (blue line) and 0.025 (red line). The first eight Bragg peaks are indicated by vertical bars and Miller indices (*hkl*).

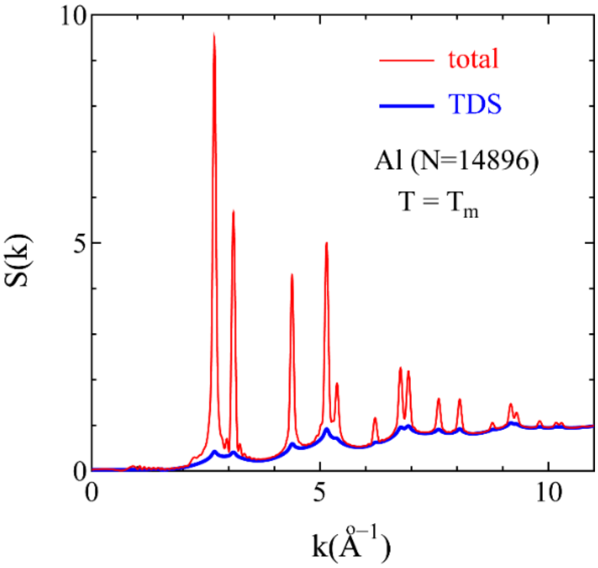

Figure 4 Total static structure factor of aluminum polycrystal at the melting point (red line). The thick blue line depicts the TDS contribution, $S_{\mathrm{TDS}}(k)$.

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By combining $S_{\mathrm{el}}(k)$ in Fig. 2 and $S_{\mathrm{TDS}}(k)$ in Fig. 3, we have calculated the total structure factor $S(k) = e^{-2W(k)}S_{\mathrm{el}}(k) + S_{\mathrm{TDS}}(k)$ of aluminum polycrystal at the melting point, which is illustrated in Fig. 4. Here, we have used the lattice constant $a = 4.05$Å and the dimensionless temperature $T_* \approx 0.025$; the latter has been estimated at the melting temperature $T = T_{\mathrm{m}} = 930$ K in conjunction with the measured Debye temperature $T_{\mathrm{D}} \equiv \hbar\bar{c}q_{\mathrm{D}}/k_B \approx 400$ K (McDonald, 1967).

Since $T_{\mathrm{m}} > T_{\mathrm{D}}$, the use of the high-temperature approximation in Eq. (6) may be valid. Apart from our arbitrary choice of the size of the crystallite, Fig. 4 qualitatively resembles the neutron powder diffraction data by Toby & Egami (1992). Although the TDS contribution is found to be small compared with Bragg peaks, it is indispensable to account for the asymptotic limits $S(k \to 0)$ and $S(k \to \infty)$.

3.3. Comparison with other theories

Meisel and Cote (1977), hereafter MC, presented a compact formula for thermal diffuse scattering applicable to all temperatures. For high temperatures $T \gg T_{\mathrm{D}}$, their formula for $S_{\mathrm{TDS}}(k)$ reads

$$S_{\mathrm{TDS}}^{\mathrm{MC}}(k) = \left[1 - e^{-2W(k)}\right]\int_0^1 d\left(\frac{q}{q_{\mathrm{D}}}\right)\int \frac{d\Omega}{4\pi} S_{\mathrm{el}}(\boldsymbol{k} + \boldsymbol{q}), \tag{24}$$

where the last integral represents an angular average of vector **q** over the solid angle Ω. To derive this expression, they first calculated the one-phonon structure factor from the general equation $S_1(\boldsymbol{k}) = (1/N)\sum_{\boldsymbol{q}} y(k,q)\, S_{\mathrm{el}}(\boldsymbol{k}+\boldsymbol{q})$, which is equivalent to (13), by introducing the approximation $y(k,q) \approx (2/3)W(k)(q_{\mathrm{D}}/q)^2\Theta(q_{\mathrm{D}} - q)$; this approximation is equivalent to setting $e^{-2W(k)} = 1$ in our one-phonon kernel (11) and hence valid only for $k \ll q_{\mathrm{D}}$. They thus obtain

$$S_1(k) = 2W(k)\int_0^1 d\left(\frac{q}{q_{\mathrm{D}}}\right)\int \frac{d\Omega}{4\pi} S_{\mathrm{el}}(\boldsymbol{k}+\boldsymbol{q}).$$

They subsequently incorporated higher-order phonon scattering approximately by replacing the factor $2W(k)$ by $1 - e^{-2W(k)}$, leading to (24). Analogous formula expressing $S_{\mathrm{TDS}}(k)$ in terms of one- and two-phonon structure factors has been given in Eq. (11.94) of Warren (1990). Thermal vibrations in metallic glass have been studied by those approximate formulae (Schönfeld *et al.*, 2017).

As for the asymptotic behaviours, the MC formula (24) satisfies the large-k limit (23) only when $S_{\mathrm{el}}(k \to \infty) = 1$, whereas Eq. (23) is ensured rather by the multiphonon kernel function $\bar{y}_{\mathrm{m}}(k,q)$ in the present theory. The MC theory may also fail to reproduce (19) in the $k \to 0$ limit unless the singular term $S_{\mathrm{el}}(0)$ at $\boldsymbol{q} = -\boldsymbol{k}$ is treated separately in Eq. (24) as we did in Eq. (18). The origin of one-phonon peaks in the intermediate-k regime is inherent in our Eq. (16), while the corresponding mechanism is less apparent in (24). We further remark that the upper limit of q-

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integration for multi-phonon scattering is set to infinity in (18); there is no reason to truncate the integral at $q = q_{\mathrm{D}}$ as in (24).

Practically, MC formula (24) involves a two-dimensional integral; the angular average of the elastic structure factor would require careful numerical procedures. In contrast, the present formula (18) requires only a one-dimensional radial integral of $S_{\mathrm{el}}(q)$, because the angular average has been imposed on the kernel function and evaluated analytically. This clearly points to an improved computational efficiency of the present formula.

4. Concluding remarks

In conclusion, we have proposed a new semianalytic formula for the static structure factor of solids at finite temperatures by taking into account multiphonon diffuse scattering to infinite order. The resultant total structure factor is given by $S(k) = e^{-2W(k)}S_{\mathrm{el}}(k) + S_{\mathrm{TDS}}(k)$, which consists of elastic and TDS parts. The elastic part should be evaluated separately. The principal outcome of this work is formula (18) for the TDS part. The derivation of our new formula is based on the observation (see Fig. 1) that the TDS beyond the one-phonon process, exposed by the short-range part of Eq. (9), can be fitted accurately by a Gaussian function. These findings enable us to obtain a compact analytic kernel function (14). The one-phonon part (15) accounts for the compressibility relation in the small-wavenumber limit as well as the peaks of TDS intensities at the Bragg points, while the multiphonon part (17) governs the convergence of the structure factor at large wavenumbers. The temperature is measured by the dimensionless parameter T_* related to the average sound speed as defined in (7). Superiority of the present formula to other theoretical models have been demonstrated in both physics contents and computational efficiency.

Our assumption of isotropic phonon dispersion in the Debye model is a crude approximation. In order to incorporate realistic phonon dispersions, we have to improve (6). In principle, the Debye-Waller factor (1) can be generalized by taking into account phonon density of states (Maradudin *et al.* 1971). Such a replacement of $W(k)$ may not be sufficient, however, since the function $\mathrm{Si}(q_{\mathrm{D}}r)/q_{\mathrm{D}}r$ in (6) should also be modified appropriately in order to keep consistency with the asymptotic properties (19) and (23). Improvement of the present theory would need further investigations.

In this work, we have studied only simple solids composed of a single species of atoms. It would be desirable to clarify the limitations of our model for more complicated systems, especially when the model is used to distinguish the TDS contribution from other types of disorder. To facilitate comparison with x-ray or neutron scattering data for multicomponent systems, it may be appropriate to incorporate the atomic form factor or neutron scattering length for each atomic species into the definition of $S(k)$ (Toby & Egami, 1992; Billinge, 2019). Formal generalization of basic equations

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(1)-(5) to ordered alloys may be straightforward (Zacharias *et al*., 2021), but the structure factors of partially disordered alloys may be influenced by order parameters characterizing correlations of atomic arrangements (Hafner, 1987). While only the Debye-type acoustic phonons have been considered as dominant contributions to TDS, soft vibration modes in certain amorphous solids should be considered as exceptions to the conventional Debye model (Hafner, 1987). Bearing these cautions in mind, we shall intend to extend our model formula (18) to complicated systems in the future.

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