Structure factors in amorphous and disordered harmonic Debye solids

L. V. Meisel and P. J. Cote
Benet Weapons Laboratory, Watervliet Arsenal, Watervliet, New York 12189
(Received 20 April 1977)

Expressions for the static and dynamic structure factor of Van Hove and for the static structure factors appropriate for x-ray and neutron scattering and for resistivity are presented in harmonic approximation for amorphous and disordered solids having a Debye phonon spectrum. A useful model dynamic structure factor containing a temperature-dependent function of K is defined. The high- and low-temperature limiting forms are examined in detail and the entire temperature dependence is discussed qualitatively. Applications in the areas of resistivity and scattering of x-rays are discussed.

I. INTRODUCTION

The dynamic structure factor $S(\vec{K}, \omega)$ introduced by Van Hove[1] can be expanded in the form

$$S(\vec{K}, \omega) = S_0(\vec{K}, \omega) + S_1(\vec{K}, \omega) + \cdots , \tag{1}$$

where in harmonic approximation

$$S_0(\vec{K}, \omega) = a(\vec{K}) e^{-2W(\vec{K})} \delta(\omega) , \tag{2}$$

and

$$\frac{S_1(\vec{K}, W)}{e^{-2W(\vec{K})}} = \frac{n(-\omega)}{-\omega} \sum_q \frac{hK^2}{2M} [a(\vec{K}+\vec{q})\delta(\omega+\omega_q) + a(\vec{K}-\vec{q})\delta(\omega-\omega_q)], \tag{3}$$

where $e^{-2W(\vec{K})}$ is the Debye-Waller factor and $q = (\vec{q}, j)$ with polarization index j, and defining $x = h\omega/kT$,

$$n(\omega) = (e^x - 1)^{-1} . \tag{4}$$

We shall use this definition of x throughout.

The structure factor $a(\vec{K})$ is defined as

$$a(\vec{K}) = \frac{1}{N} \sum_{n,m} \exp[i\vec{K} \cdot (\vec{m} - \vec{n})] . \tag{5}$$

Systematic theoretical investigation of $S(\vec{K}, \omega)$ in crystalline solids and liquids has proven highly enlightening.[2] Furthermore, as is well known, $S(\vec{K}, \omega)$ is directly accessible to experiment. Disordered and amorphous solids have continuous structure factors $a(\vec{K})$ which yield physical effects different from those occurring when $a(\vec{K})$ is a sum of δ functions.

It has proven useful to define static structure factors appropriate for various physical processes. In this work we will be interested in the static structure factor appropriate for x-ray or neutron scattering, $S^x(\vec{K})$, and the static structure factor appearing in Ziman's expression for the electrical resistivity $S^\rho(\vec{K})$. These functions are defined as

$$S^x(\vec{K}) = \int_{-\infty}^{\infty} S(\vec{K}, \omega) d\omega \tag{6}$$

and

$$S^\rho(\vec{K}) = \int_{-\infty}^{\infty} S(\vec{K}, \omega) x n(x) d\omega . \tag{7}$$

We shall attempt to elucidate the properties of the various structure factors arising in the study of glassy and disordered solids and will discuss a model dynamic structure factor $S_M(\vec{K}, \omega)$ proposed in a previous publication.[3] We shall assume a Debye phonon spectrum throughout the sequel.

II. STATIC STRUCTURE FACTORS FOR A HARMONIC APPROXIMATION DEBYE SOLID

For a Debye solid Eqs. (3) and (6) yield

$$S_1^x(\vec{K}) = \frac{hK^2}{2M} \sum_q \omega_q^{-1} [a(\vec{K}-\vec{q})(n_q+1) + a(\vec{K}+\vec{q})n_q]$$
$$= \alpha(K) \int_0^1 \left(\frac{q}{q_D}\right) d\left(\frac{q}{q_D}\right) [n(x) + \tfrac{1}{2}] \int \frac{d\Omega}{4\pi} a(\vec{K}+\vec{q}) . \tag{8}$$

Similarly Eqs. (3) and (7) yield

$$S_1^\rho(\vec{K}) = -\frac{hK^2}{2M} \sum_q \frac{h}{kT} [a(\vec{K}+\vec{q}) + a(\vec{K}-\vec{q})] n(x) n(-x)$$
$$= -\alpha(K)(\Theta/T) \int_0^1 \left(\frac{q}{q_D}\right)^2 d\left(\frac{q}{q_D}\right) n(x) n(-x) \times \int \frac{d\Omega}{4\pi} a(\vec{K}+\vec{q}) . \tag{9}$$

In these integrals $x = h\omega_q/kT = (h\omega_D/kT)(q/q_D) = (\Theta/T)q/q_D$. The abbreviation $\alpha(\vec{K}) = 3(hK)^2 e^{-2W(K)}/Mk\Theta$ will be used throughout. Given a structure factor $a(\vec{K})$ and a Debye temperature Θ, Eqs. (8) and (9) allow computation of the static structure factors to arbitrary precision. However, we shall proceed in a general way.

III. HIGH-TEMPERATURE FORMS

At high temperatures $n(x) \approx -n(-x) \approx x^{-1} \gg 1$ for most q values in the integral of Eqs. (8) and

(9). Thus,

$$S_1^{\rho}(K) = S_1^{x}(K) \rightarrow \alpha(K)\frac{T}{\Theta}\int_0^1 d\left(\frac{q}{q_D}\right)\int \frac{d\Omega}{4\pi}\, a(\vec{K}+\vec{q}) . \quad (10)$$

The integral in Eq. (10) averages $a(\vec{K})$ over a region within q_D of $\vec{K}$. This average will effectively smooth out the variations in $a(\vec{K})$ and approach its average value of unity.

IV. LOW-TEMPERATURE FORMS

At low temperatures $n(x) \ll 1$ for most q values. Thus, in Eq. (8) for the x-ray static structure factor the zero-point motion term will dominate and

$$S_1^{x}(K) \rightarrow \tfrac{1}{4}\alpha(K)\int_0^1 2\left(\frac{q}{q_D}\right)d\left(\frac{q}{q_D}\right)\int \frac{d\Omega}{4\pi} a(\vec{K}+\vec{q}) . \quad (11)$$

The integral in Eq. (11) is a weighted average of $a(\vec{K})$ over a region within q_D which will again approach unity at all $\vec{K}$.

In Eq. (9), on the other hand, there is no zero-point term and the presence of the $n(x)$ factor will cause the dominant contributions to the integral to come from regions of small q, i.e., the average of the structure factor will be over only a small region near $\vec{K}$ rather than over all values within q_D of $\vec{K}$. Thus, we can make a Taylor expansion of $a(\vec{K}+\vec{q})$ about $a(\vec{K})$ and neglect higher-order terms:

$$a(\vec{K}+\vec{q}) = a(\vec{K}) + \vec{q}\cdot\nabla_{\vec{K}}\, a(K) + \tfrac{1}{2}\vec{q}\vec{q}:\nabla_k\nabla_k\, a(\vec{K}) + \cdots . \quad (12)$$

For glassy materials $a(\vec{K}) \approx a(K)$ and so

$$\int \frac{d\Omega}{4\pi}\, a(\vec{K}+\vec{q}) = a(K) + \left(\frac{q}{q_D}\right)^2 a^{II}(K) + \cdots , \quad (13)$$

where

$$a^{II}(K) = \tfrac{1}{3}[a''(K) + 2a'(K)/K] , \quad (14)$$

with differentiation with respect to K indicated by prime. Thus,

$$S_1^{\rho}(\vec{K}) = \alpha(K)(T/\Theta)^2[a(K)I_1(\Theta/T) + a^{II}(K)(T/\Theta)^2 \times I_4(\Theta/T) + \cdots] , \quad (15)$$

where

$$I_n(X) \equiv \int_0^X x^n n(x) n(-x) dx . \quad (16)$$

V. MODEL DYNAMIC STRUCTURE FACTOR

We have shown how the various averages of the structure factor $a(K)$ play a role in determining the static structure factors. We are thus led to define a model dynamical structure factor $S_M(\vec{K}, \omega)$ containing a temperature-dependent averaged structure factor $A(K)$.[3] In analogy with Eq. (1) define

$$S_M(\vec{K}, \omega) \equiv S_0(\vec{K}, \omega) + S_{M,1}(\vec{K}, \omega) + \cdots , \quad (17)$$

where $S_0(\vec{K}, \omega)$ is defined in Eq. (2) and

$$S_{M,1}(\vec{K}, \omega) \equiv \begin{cases} \frac{1}{2}\frac{h}{kT}\,\alpha(K)\left(\frac{T}{\Theta}\right)^2 \frac{x}{1-e^{-x}}\, A(\vec{K}) , & |x| \le \frac{\Theta}{T} \\ 0, & |x| > \frac{\Theta}{T} . \end{cases} \quad (18)$$

$S_{M,1}(\vec{K}, \omega)$ as been constructed in analogy with Eq. (3) and satisfies the detailed balance condition and gives the proper x-ray and neutron static structure factors. This will be shown next.

VI. X-RAY AND NEUTRON SCATTERING

Integration of Eq. (6) using (17) and (18) yields

$$S_M^{x}(K) = a(K)e^{-2W(K)} + \alpha(K)(T/\Theta)^2 I(\Theta/T)A^{x}(K) + \cdots$$

$$= a(K)e^{-2W(K)} + 2W(K)A^{x}(K) + \cdots \quad (19)$$

$$\approx a(K)e^{-2W(K)} + A^{x}(K)(1 - e^{-2W(K)}), \quad (20)$$

where

$$I(X) = \int_0^X x(n(x) + \tfrac{1}{2}dx , \quad (21)$$

and $\alpha(K)(T/\Theta)^2 I(\Theta/T)$ is the exponent in the Debye-Waller factor. The form expressed in Eq. (20) is a generalization of the Debye independent oscillator expression,[4] which is often assumed for structurally disordered systems.[5-7] Our analysis indicates that $A^{x}(K)$ is a coarse average of the structure factor $a(K)$ at all temperatures. In particular at high temperatures

$$A^{x}(K) \rightarrow \int_0^1 d\left(\frac{q}{q_D}\right)\int \frac{d\Omega}{4\pi}\, a(\vec{K}+\vec{q}) , \quad (22)$$

and at low temperatures

$$A^{x}(K) \rightarrow \int_0^1 2\left(\frac{q}{q_D}\right)d\left(\frac{q}{q_D}\right)\int \frac{d\Omega}{4\pi}\, a(\vec{K}+\vec{q}) . \quad (23)$$

VII. ELECTRICAL RESISTIVITY

Integration of Eq. (7) using (17) and (18) yields

$$S_M^{\rho}(K) = a(K)e^{-2W(K)} + \alpha(K)(T/\Theta)^2 I_2(\Theta/T)A^{\rho}(K) . \quad (24)$$

We have used this form in a previous publication[3] to explain the T^2 dependence of the electrical resistivity observed in numerous disordered and glassy metals at low temperatures. In that publication we stated that at low temperatures $A^{\rho}(K)$ goes to the ordinary structure factor at low temperatures and that at high temperatures it approaches unity. This can be verified by examina-

tion of Eqs. (10), (15), and (24). At high temperatures

$$A^{\rho}(K) \rightarrow \int_0^1 d\left(\frac{q}{q_D}\right) \int \frac{d\Omega}{4\pi}\, a(\vec{K}+\vec{q}) \approx A^{x}(K)\,. \qquad (25)$$

$A^{\rho}(K)$ is a coarse average of the structure factor $a(K)$ and is therefore approximately equal to unity for all K. At low temperatures

$$A^{\rho}(K) = a(K) + (T/\Theta)^2 a^{II}(K) I_4(\Theta/T)/I_2(\Theta/T) + \cdots \qquad (26)$$

which goes to $a(K)$ at $T=0$. We also see that the deviations go as $(T/\Theta)^2$ at low temperatures.

We see that $A^{\rho}(K)$ varies from $a(K)$ at absolute zero to a coarse-grained average of the structure factor at high temperatures in a continuous manner.

VIII. CONCLUSIONS AND SUMMARY

(i) In harmonic approximation with a given phonon spectrum Eqs. (3)–(7) can be used to compute static structure factors at any temperature. For a Debye solid, Eqs. (8) and (9) can be used to compute static structure factors at arbitrary temperature. Limiting expressions valid at high and low temperatures are provided in Eqs. (10), (11), and (15).

(ii) The model dynamic structure factor defined in Eqs. (2), (17), and (18) provides a useful framework for the analysis of x-ray and neutron scattering experiments and resistivity studies in amorphous and disordered materials.

(iii) For x-ray or neutron scattering the averaged structure factor $A(K)$ appearing in the model dynamic structure factor is a coarse-grain average of the structure factor $a(K)$ within q_D of the argument $\vec{K}$ at all temperatures, i.e., $A^{x}(K) \approx 1$ at all temperatures in amorphous and disordered solids.

(iv) For resistivity, the averaged structure factor $A^{\rho}(K) = a(K)$ at $T=0$ with deviations going like $(T/\Theta)^2$ at low temperatures. At high temperatures $A^{\rho}(K) \approx A^{x}(K) \approx 1$. Thus, as temperature is increased $A^{\rho}(K)$ goes over smoothly from the generally highly structured function $a(K)$ at $T=0$ to a coarse-grained average of $a(K)$ at high temperatures.

(v) The approximate form for the static structure factor for x-ray or neutron scattering given in Eq. (20) is given a physical basis in terms of the averaged structure factor $A^{x}(K)$ defined here. One sees that for amorphous materials a rough approximation may be obtained at all temperatures by substituting unity for $A^{x}(K)$ in Eq. (20).

(vi) As previously reported,[3] for any metal whose structure can be represented by a continous $a(q)$, the low-temperature resistivity varies as T^2 rather than T^5 and at high temperatures, the resistivity should vary linearly in T as in the crystalline case.

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