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LIGHT SCATTERING FROM CRYSTALS, GLASSES AND LIQUIDS *

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ABSTRACT

The theory of inelastic light scattering from a model system in the crystalline, disordered and liquid phases is analyzed. The roles of disorder induced first order scattering and second order scattering are clarified in the context of the classical liquid. The correlation functions appropriate for the various contributions are identified and useful ways of processing experimental data are pointed out.

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Inelastic light scattering (i.e., Brillouin and Raman scattering) from phonons in crystalline solids¹ and internal vibrational modes in molecules² are very well understood. Since the initial work of Shuker and Gammon³ much progress has been made in the theoretical analysis of light scattering from amorphous solids as well.^{4,5} By contrast, the analysis of the inelastic or quasi-elastic light scattering from particle motion in atomic or ionic liquids is still not very well developed.⁶ Although much advance has been made in the case of inert element liquids with the use of numerical simulation methods, no clear-cut prescriptions for useful ways of "reducing" experimental data have evolved. For instance, the Raman spectra of molten alkali halides have been analyzed both from the point of view of second order processes⁷ and that of disorder induced first order phonon scattering.⁸ A similar dichotomy exists with respect to the interpretation of Raman scattering from certain superionic conductors.⁹ The purpose of this report is to clarify the relationship between the two types of analyses. This will also help identify what thermal and frequency factors, if any, should be divided out of the raw data in order to extract the dynamical information in the spectra.

We treat the scattering of light from the simplest possible model system in the crystalline, amorphous, and liquid phases. The model we consider is that of an assembly of neutral, polarizable, point particles. Our treatment closely parallels the work of Werthamer¹⁰ for the solid, Stephen¹¹ for the liquid, and Jäckle for the amorphous phase.⁵

Consider an assembly of N particles of polarizability α . No assumption is made at this stage concerning the structure of the system. The scattering efficiency is proportional to the power spectrum of the fluctuating part of the dielectric susceptibility tensor¹:

$$Z_{IS}(\vec{q}, \omega) = \int dt e^{i\omega t} \langle \chi_{IS}(\vec{q}, t) \chi_{IS}^*(\vec{q}, 0) \rangle . \quad (1)$$

Here $\chi_{IS} = \hat{n}_I \cdot \vec{\chi} \cdot \hat{n}_S$, where \hat{n}_I and \hat{n}_S are, respectively, the directions of polarizations of the incident and scattered light. We write

$$\chi_{\mu\nu}(\vec{q}, t) = \sum_{i=1}^N e^{i\vec{q} \cdot \vec{R}_i(t)} A_{\mu\nu}^{(i)}[\{\vec{R}\}] , \quad (2)$$

where the effective polarizability $A_{\mu\nu}^{(i)}$ of the i^{th} particle implicitly depends on the positions and histories (through retardation effects) of all other particles. We will proceed by introducing considerable simplicity at the expense of unnecessary rigor.^{12,13} Thus, we assume that $A_{\mu\nu}^{(i)}$ depends only on the instantaneous positions of all other particles. This is reasonable if the mutual polarizability is short ranged as we will assume here. In addition to the isolated atom polarizability (α) there are contributions from pairs, triplets, etc.¹² Restricting to pair contributions, we have

$$A_{\mu\nu}^{(i)}(t) = \alpha \delta_{\mu\nu} + \frac{1}{2} \sum_j' T_{\mu\nu}[\vec{R}_i(t), \vec{R}_j(t)] + \dots , \quad (3)$$

with the pair or "bond" polarizability given by

$$T_{\mu\nu}(\vec{r}) = \alpha^2 [3r_{\mu}r_{\nu} - r^2 \delta_{\mu\nu}] / r^5 . \quad (4)$$

Since we have assumed that the particles are polarizable point particles we have just the dipole-induced dipole effect above. A more general form would add an isotropic term as well.

Let us first consider the term proportional to α in Eq.(3). The scattering efficiency due to this term is proportional to

$$Z_{IS}^{(1)}(\vec{q}, \omega) = \delta_{IS} \alpha^2 S(\vec{q}, \omega) , \quad (5)$$

where $S(\vec{q}, \omega)$ is the usual dynamic structure factor

$$S(\vec{q}, \omega) = \int dt e^{i\omega t} \left\langle \frac{1}{N} \sum_i \sum_j e^{i\vec{q} \cdot \vec{R}_i(t)} e^{-i\vec{q} \cdot \vec{R}_j(0)} \right\rangle. \quad (6)$$

This is the same function that governs neutron scattering.¹⁴ However, here we are dealing with $q \approx 10^5 \text{ cm}^{-1}$, not accessible to neutron scattering. Such small wavevectors are inaccessible to numerical simulation studies as well. However, this is the hydrodynamic regime where a continuum description is appropriate. Not surprisingly, there is not much qualitative difference in the light scattering from the three phases in this mechanism. The Brillouin scattering arises from the propagating sound waves in the medium. In the liquid $S(\vec{q}, \omega)$ is analyzed in terms of density fluctuations. The long wavelength density fluctuations, namely longitudinal sound waves, are underdamped in the $q \rightarrow 0$ limit (viscous damping goes like q^2).⁶ Thus, the usual Brillouin peaks are expected in the liquid.

For the harmonic solid (crystalline and amorphous) the atomic positions may be expanded about their equilibrium positions, and the displacements expressed in terms of normal modes:

$$\vec{R}_i(t) = \vec{R}_i^{(0)} + \vec{u}_i(t) \quad (7)$$

$$\vec{u}_i(t) = \sum_{\vec{k}\lambda} \left(\frac{\hbar}{M\omega_{\vec{k}\lambda}} \right)^{1/2} \sum_{\vec{k}\lambda} \hat{\xi}_{\vec{k}\lambda} f_{\vec{k}\lambda}(\vec{R}_i^{(0)}) Q_{\vec{k}\lambda}(t), \quad (8)$$

where $\hat{\xi}_{\vec{k}\lambda}$ is the polarization unit vector for the normal mode, and $Q_{\vec{k}\lambda}(t)$ is the normal mode coordinate. For the crystal $f_{\vec{k}\lambda}(\vec{R}_i^{(0)})$ is a plane wave, while for the amorphous solid it is an attenuated wave. In the one phonon or first order approximation the single particle polarizability contribution becomes

$$Z_{IS}^{(1)}(\vec{q}, \omega) = \alpha^2 \delta_{IS} \frac{\hbar}{M\omega} [n(\omega)+1] \sum_{\lambda} \delta(\omega - \omega_{\vec{q}\lambda}) \left| \vec{q} \cdot \hat{\xi}_{\vec{q}\lambda} \right|^2, \quad (9)$$

for the crystal and

$$Z_{IS}^{(1)}(\vec{q}, \omega) = \alpha^2 \delta_{IS} \frac{\hbar}{M\omega} [n(\omega)+1] \sum_{\vec{k}\lambda} \delta(\omega - \omega_{\vec{k}\lambda}) \vec{q} \cdot \hat{\xi}_{\vec{k}\lambda} \vec{q} \cdot \hat{\xi}_{\vec{q}-\vec{k}, \lambda} C_{\lambda}(\vec{q}-\vec{k}), \quad (10a)$$

where

$$C_{\lambda}(\vec{q}-\vec{k}) = \sum_i \sum_j e^{i\vec{q} \cdot (\vec{R}_i^{(0)} - \vec{R}_j^{(0)})} f_{\vec{k}\lambda}(\vec{R}_i^{(0)}) f_{\vec{k}\lambda}^*(\vec{R}_j^{(0)}) \quad (10b)$$

For the crystal only the acoustic modes near the zone center scatter. For the amorphous solid we see that modes of all wave vectors may scatter by virtue of the finite mean free path of the phonons. This is the so-called "mechanical disorder".⁵ In both Eq.(9) and Eq.(10) the factor $[n(\omega)+1] \hbar/\omega$ is approximately $k_B T / \omega^2$ so that the scattering efficiency is controlled by the factor $k_B T q^2 / \omega^2$. Hence, acoustic modes ($\omega \approx c_s q$) scatter much more strongly than modes of slower than linear dispersion and the usual Brillouin peaks are recovered.

We now turn to the pair or "bond" polarizability term in Eq.(3) which is of main interest here. Once again, in the interest of simplicity approximations appropriate for $q \approx 0$ and $T(R) \sim R^{-3}$ will be made. The scattering efficiency is proportional to

$$Z_{IS}^{(2)}(\vec{q}, \omega) = \int dt e^{i\omega t} \left\langle \sum_{i \neq j} \sum_{l \neq m} e^{i\vec{q} \cdot [\vec{R}_i(t) - \vec{R}_j(0)]} T_{IS}[\vec{R}_i(t) - \vec{R}_j(t)] T_{IS}(\vec{R}_i(0) - \vec{R}_m(0)) \right\rangle. \quad (11)$$

Upon taking Fourier transform of $T(\vec{R})$ this may be written as

$$Z_{IS}^{(2)}(\vec{q}, \omega) = \int dt e^{i\omega t} \int d^3h \int d^3k' T(\vec{k}) T^*(\vec{k}') \left\langle n_{\vec{q}-\vec{k}}(t) n_{\vec{k}}(t) n_{\vec{k}-\vec{q}}(0) n_{-\vec{k}}(0) \right\rangle, \quad (12a)$$

where

$$n_{\vec{k}}(t) = \sum_j e^{i\vec{k} \cdot \vec{R}_j(t)} \quad (12b)$$

The pair polarizability contribution leads to the consideration of four point density correlations.¹² Except in the case of a harmonic solid these are evaluated either by a decoupling ansatz,¹¹ by numerical simulation,⁶ or by appeal to lattice gas models.¹⁵

Since our purpose here is merely to clarify the difference between light scattering from the three phases, a decoupling scheme suffices. One way to motivate the decoupling is to transform the four particle coordinates into two bond centers and two bond vectors. The decoupling then amounts to assuming that the bond center density fluctuations are uncorrelated with the bond length fluctuations. In a dilute, associated (i.e., molecular) fluid such a decoupling is, of course, well justified. Here we adopt it only for purpose of illustrations. Then, we can reduce Eq.(12) to¹¹

$$Z_{IS}^{(2)}(\vec{q}, \omega) = \int d^3k \int d\omega' |T_{IS}(\vec{k})|^2 S(\vec{k}, \omega') S(\vec{q}-\vec{k}, \omega-\omega'). \quad (13)$$

We will now examine the prediction of Eq.(13) for the three phases.

For an ordered, crystalline solid we have

$$S(\vec{k}, \omega) = \frac{N}{V} \delta(\vec{k}) \delta(\omega) + \frac{\hbar}{M\omega} [n(\omega)+1] \sum_{\lambda} \delta(\omega-\omega_{\vec{k}\lambda}^{\sigma}) \left| \sum_{\sigma\sigma'} \vec{k} \cdot \left(\frac{\hat{\alpha}_{\sigma\lambda}^{\sigma}}{\xi_{\vec{k}\lambda}^{\sigma}} - \frac{\hat{\alpha}_{\sigma\lambda}^{\sigma'}}{\xi_{\vec{k}\lambda}^{\sigma'}} e^{i\vec{k} \cdot \vec{r}_{\sigma\sigma'}} \right) \right|^2, \quad (14)$$

where we have retained the zero and one phonon terms. Here $\vec{r}_{\sigma\sigma'} = \vec{r} + \vec{a}_{\sigma\sigma'}$, where \vec{r} is a Bravais lattice vector and $\vec{a}_{\sigma\sigma'}$ is a nonprimitive vector from atom σ to atom σ' in the unit cell. Substituting Eq.(14) into Eq.(13) and neglecting the purely elastic contribution, we get

$$Z_{IS}^{(2)}(\vec{q}, \omega) = [Z_{IS}^{(2)}]_1 + [Z_{IS}^{(2)}]_2 + \dots, \quad (15)$$

with the one-phonon term given, after some manipulation, by

$$[Z_{IS}^{(2)}]_1 = \frac{\hbar}{M\omega} [n(\omega)+1] \sum_{\lambda} \delta(\omega-\omega_{\vec{q}\lambda}^{\sigma}) \left| \sum_{\sigma\sigma'} \left(\frac{\hat{\alpha}_{\sigma\lambda}^{\sigma}}{\xi_{\vec{q}\lambda}^{\sigma}} - \frac{\hat{\alpha}_{\sigma\lambda}^{\sigma'}}{\xi_{\vec{q}\lambda}^{\sigma'}} e^{i\vec{q} \cdot \vec{r}_{\sigma\sigma'}} \right) \cdot \vec{\nabla} T_{IS}(\vec{r}_{\sigma\sigma'}) \right|^2, \quad (16)$$

There is a corresponding expression for the two-phonon or second order scattering involving $\vec{\nabla} \vec{\nabla} T$.¹⁰ For a non-Bravais crystal Eq.(16) gives the familiar Raman scattering from zone-center modes of optic character. For centrosymmetric crystals the first order scattering vanishes.

A comment is in order concerning the distinction between "second order" scattering and "pair polarizability" scattering. The term "order" usually refers to the number of phonons created (or annihilated) during the scattering process. Thus, Eq.(13) which includes all pair polarizability effects contains first order, second order, etc. phonon processes. The confusion often arises since the structure of the approximate expression, Eq.(13) leads to viewing the scattering as arising from pairs of excitations of wavevectors \vec{k} and $\vec{q}-\vec{k}$. In the crystal the first order scattering arises from the cross term between the zero and one phonon parts of the dynamic structure factors. We shall return to this point later. In the two phonon scattering (second order process) modes of all wavevectors scatter, but the short range nature of $T(R)$ tends to emphasize the zone edge modes. Thus, second order spectra are usually dominated by zone edge critical points.

Turning to the amorphous solid we may write in place of Eq.(14)

$$S(\vec{k}, \omega) = S(\vec{k}) \delta(\omega) + [n(\omega)+1] \frac{\hbar}{M\omega} \sum_{\vec{k}'\lambda} G_{\lambda}(\vec{k}-\vec{k}') \delta(\omega-\omega_{\vec{k}'\lambda}^{\sigma}), \quad (17)$$

where we have once again retained only zero and one phonon contributions as before. $S(\vec{k})$ is the static structure factor, and the second term displays the "mechanical disorder" explicitly as discussed above. Substituting Eq.(17)

into Eq.(13) we get for the one phonon contribution

$$\left[z_{rs}^{(2)} \right]_1 = [n(\omega) + 1] \frac{\hbar}{M\omega} \sum_{\vec{k}} |T(\vec{k})|^2 S(\vec{k}-\vec{k}') \sum_{\vec{k}'\lambda} G_{\lambda}(\vec{k}'-\vec{k}) \delta(\omega - \omega_{\vec{k}'\lambda}). \quad (18)$$

We now see the effect of "electrical disorder"^{5,16} through the presence of the static structure factor. Thus, even in the absence of mechanical disorder modes of all wavevectors may scatter.⁵

It is clear from the above discussion that disorder induced first order scattering arises from the presence of the zero-frequency component of the dynamic structure factor. Unlike the amorphous solid the liquid $S(\vec{k}, \omega)$ has no $\delta(\omega)$ term in it. Thus, the pair polarizability scattering in the liquid cannot give rise to the $S(\vec{k}) S(-\vec{k}, \omega)$ contribution which represents the static disorder induced first order scattering. The reduction of experimental data by the factor $\omega / [n(\omega) + 1]$ is natural for the low temperature amorphous solid³ but not for the liquid.

In comparing the spectrum below the melting point with that above in the inert elements¹⁷ it was noticed that the high frequency shift part of the spectrum was hardly affected, while the lower frequency region showed an increase in intensity upon melting. Further, in the alkali halide melts reduction of the spectra as in amorphous solids produces a peak at a frequency which corresponds to the Debye frequency in the solid.⁸ It is thus, tempting to make the analysis of the melt spectrum in terms comparable to that of the solid. This may be accomplished in a qualitative way by (a) separating out the diffusive and oscillatory components of the motion, and (b) describing the oscillatory motion as damped, harmonic, quantum oscillators. Then we may write

$$S_D(\vec{k}, \omega) \approx S(\vec{k}) \frac{\gamma_{\vec{k}}^2}{\omega^2 + \gamma_{\vec{k}}^2}, \quad (19)$$

$$S_V(\vec{k}, \omega) \approx \frac{\hbar [n(\omega) + 1]}{\omega} f(\omega - \omega_{\vec{k}}) \quad (20)$$

where $f(\omega)$ might be, e.g., a Lorentzian. It is clear that the cross term between these two components when substituted into Eq.(13) will lead to a term similar to "disorder induced" first order scattering.

On the basis of the behavior suggested by Eqs.(19) and (20) we may divide the liquid state spectrum crudely into three frequency regions: (a) $\omega \lesssim Dk_0^2$, where D is the diffusion constant and k_0 is the wavevector for which $|T(\vec{k})|^2$ has its maximum. The spectrum here is a signature of purely diffusive motion. (b) $\omega \lesssim \omega_{\max}$, where ω_{\max} is the maximum phonon frequency in the high temperature solid. The spectrum in this region may be viewed as a signature of the homogeneously broadened one phonon density of states, although two phonon difference type of processes are also important. (c) $\omega_{\max} \lesssim \omega \lesssim 2\omega_{\max}$, where the spectrum is most likely to be similar to the two phonon overtone spectrum in the solid below the melting point. Contributions (a) and (b) are "turned on" upon melting and may account for the entire difference between the solid and melt spectra in the case of the inert elements.¹⁸

In conclusion, we have shown that within the pair polarizability approximation the resulting four-particle correlation function describes both the disorder induced first order scattering and the usual second order scattering from pairs of excitations. In the liquid these remain qualitative concepts and do not lend themselves to any natural frequency prefactors as in the case of amorphous solids. A further complication not considered here is the possibility of a new mechanism for coupling of light to fluctuations in the system

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which is dominant in the liquid only. For instance, in ionic melts there are strong, fluctuating electric fields that may give rise to light scattering through nonlinear susceptibilities.¹⁹ Similar concepts have been invoked by Cazzanelli et al.²⁰ to explain the light scattering from α -AgI.

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