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Vibrational density of states measurements in disordered systems

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Abstract. We present a data treatment procedure, based on an iterative technique, properly developed to subtract the multi-phonon contributions from the dynamic structure factor in a self-consistent way. With this technique, we derive the one-phonon vibrational density of states from the dynamic structure factor of different disordered systems, in the framework of the incoherent scattering approximation. We present results on glassy glucose ($C_6H_{12}O_6$), a nearly perfect incoherent scatterer, due to high hydrogen content. The data treatment procedure has been found to work well also for the more complex case of dry and hydrated DNA.

1. Introduction

Neutron Scattering is a useful technique to access the atomic dynamics of solids. The density of states (v-DOS) is an important quantity obtainable by inelastic neutron scattering data, because it provides the weight of each frequency, or energy, of the vibrational modes. Nevertheless working out the v-DOS from the measured double differential cross section can be a rather difficult task. Indeed a wide range of custom techniques is found in literature, depending on the system under investigation and on the particular characteristics of the experiment. When the system can be reasonably approximated as an incoherent scatterer, the incoherent one-phonon approximation can be safely used to work out the v-DOS from the dynamic structure factor, in the limit where the multi-phonon contributions are negligible [1]. Unfortunately the most common systems have both coherent and incoherent cross sections. In principle the incoherent approximation is valid in coherent systems when the correlations between atomic motions can be ignored, that is at high enough wave vector transfer [2, 3], however in such a limit the multiphonon contribution cannot be neglected [1, 4, 5]. Usually experiments are performed at smaller wave vector transfer for reasons of intensity, available dynamic range or other questions concerning the physical problem under investigation. This makes the data analysis difficult and often requires a comparative investigation with molecular dynamic simulations [6]. Of course the double differential cross section includes several contributions from modes of different microscopic origin, especially when treating data from experiments on multi-component and macromolecular systems. In these cases, librational and vibrational modes belonging to specific and bound atomic groups contribute to the v-DOS, because their eigenfrequencies can be

comparable to that of the translational ones [7, 8]. From a more general point of view, it is interesting to stress that the true v-DOS is in general different from that obtained from a straightforward analysis of the inelastic neutron scattering experiments [9], which often does not consider the limits of the one-phonon incoherent approximation. We discuss here the details of an iterative technique to derive the v-DOS from neutron inelastic data and present the results of its application to two different topologically disordered systems: glassy glucose and DNA from salmon testes. Details of the performed experiments will be presented in separated papers, but a description can also be found in ref.[10].

2. Methods

Firstly we introduce the incoherent intermediate scattering function:

$$F_{inc}(Q, t) = \int_{-\infty}^{+\infty} \cos(\omega t) S_{inc}(Q, \omega) d\omega \quad (1)$$

defined as the time Fourier transform of the incoherent dynamic structure factor:

$$S_{inc}(Q, \omega) = \frac{1}{\pi} \int_0^{+\infty} \cos(\omega t) F_{inc}(Q, t) dt. \quad (2)$$

In the incoherent approximation, the dynamic structure factor (Eq.(1) and Eq.(2)) accounts for single-particle motions under the assumption that each vibrational unit of mass M has a Gaussian-distributed time-dependent displacement from its equilibrium position, $\gamma(t)$. In the case that only harmonic vibrational motions are present, the relation between $\gamma(t)$ and the v-DOS $g(\omega)$ can be derived from the Bloch identity [11] as

$$\gamma(t) = \frac{k_B T}{M} \int_0^{+\omega_M} (1 - \cos(\omega t)) n(\omega) \frac{g(\omega)}{\omega^2} d\omega \quad (3)$$

where ω_M is the upper experimental available frequency and $n(\omega)$ is the Bose occupation number. The intermediate scattering function is then obtained as:

$$F_{inc}(Q, t) = \exp(-Q^2 \gamma(t)). \quad (4)$$

To apply the approximation to measured data, the first step is the calculation of a guess $g(\omega)$ from the low angle data. Indeed at the lower scattering angles which are available in the actual experiments, contaminant multi-phonon processes are minimized and the one-phonon can therefore be roughly approximated by the total measured one. This allows to deduce the $g(\omega)$ directly from the experimental dynamic structure factor, using the rigorous result for a cubic crystal and for fully isotropic systems:

$$S_{inc}^{+1}(Q, \omega) = Q^2 e^{(-2W)} \frac{k_B T}{2M} n(\omega) \frac{g(\omega)}{\omega}, \quad (5)$$

where e^{-2W} is the Debye-Waller factor. The guess $g(\omega)$ permits to calculate back the theoretical one-phonon dynamic structure factor by means of the Eq.(5) and the total one through the sequential use of Eq.(3), Eq.(4) and Eq.(2), at all desired wavevector transfers and scattering angles. Thus an estimation of the multiphonon contributions can be obtained by trivially calculating the difference between them. Indeed the peculiar aspect of the technique is the subtraction of multiphonon terms from the total dynamic structure factor. This is achieved through a specifically developed iterative procedure which minimizes the difference between the

total measured dynamic structure factor $S^{exp}(Q, \omega)$, and the calculated one. That means simply to require, omitting the Q - and ω -dependences for clarity:

$$S^{exp} = S_{inc} = S_{inc}^{+1} + (S_{inc} - S_{inc}^{+1}) \quad (6)$$

which implies that $S_{inc}^{+1}(Q, \omega)$ must be

$$S_{inc}^{+1} = S^{exp} - (S_{inc} - S_{inc}^{+1}). \quad (7)$$

Thus a new $S_{inc}^{+1}(Q, \omega)$ is obtained by means of Eq.(7) and the latter gives a new $g(\omega)$ through Eq.(5). The $g(\omega)$ thus derived can be used to calculate again $S_{inc}^{+1}(Q, \omega)$ and $S_{inc}(Q, \omega)$. When we applied this method to real experiments we found that the procedure rapidly converges so that a small number of iterations is necessary. Thus the calculated v-DOS has been derived self-consistently with the experimental dynamic structure factor, in such a way that the so-derived $g(\omega)$ can be used to describe the experimental dynamic structure factor in all the dynamic range. In case a good description of the experimental data is obtained, this also yields further support to the incoherent approximation, the validity of which is assumed as starting point of the adopted procedure.

3. Application to prototype disordered systems

We applied the iterative technique to work out the v-DOS from neutron data on two different disordered systems: glassy glucose and DNA. The use of the incoherent approximation is justified by the high incoherent cross-section of hydrogen atoms, largely and uniformly present in both systems. The mass term in Eq.(3) and Eq.(5) was treated as a fitting parameter during the application of the iterative technique (see below for details). As stated before the present investigations involved two different inelastic neutron scattering (INS) experiments on glucose and DNA. Both experiments were performed using the INS Time-Of-Flight (TOF) spectrometer IN4 at the Institute Laue Langevin (Grenoble, France). In the case of glucose, an incident energy of 16.88 meV was used. The resulting resolution was a gaussian-shaped function with full-width at half-maximum (FWHM) of 1.2 meV. The sample holder was an aluminium hollow cylinder of dimensions: 29 mm height, 14 mm inner diameter, and 16 mm external diameter. In the case of DNA data were acquired at two different incident neutron energies of about 67.5 and 4.8 meV, on both dry and hydrated DNA. The two instrumental setups have an energy resolution of 3.5 and 0.8 meV respectively. Only data at 67.5 meV incident energy are considered in this paper. The INS data treatment included the standard procedure: subtraction of empty container, correction for the absorption coefficient and for energy dependence of detectors efficiency, normalization to vanadium used as an elastic incoherent scatterer. Measurements were performed at 300 K for glucose and 100 K for dry and hydrated DNA, in order to work in a region where the system is far away from the melting point. Figure 1 shows the v-DOS obtained for the glucose sample, with the method described in the previous section. The comparison with the spectrum measured by Raman spectroscopy [12] displays that only a minor contribution from molecular internal motions is included in the measured v-DOS. The reduced v-DOS $\frac{g(\omega)}{\omega^2}$ as a function of ω is also displayed in figure 1. The plot shows clearly the presence of a broad excess of modes with respect to the Debye v-DOS calculated as $g_D(\omega) = \frac{3\omega^2}{\omega_D^3}$, where ω_D was obtained like in ref. [13], by means of the longitudinal and transverse velocities measured by ultrasound techniques ($v_L = 3200m/s$ and $v_T = 2200m/s$). Absolute normalization is obtained by the use of the hydrogen mass in Eq.(3) and Eq.(5). This value has been obtained as a fitting parameter resulting from the iterative routine and corresponds to the expected value of 1 atomic units. Indeed the present v-DOS is projected onto the hydrogen sites.

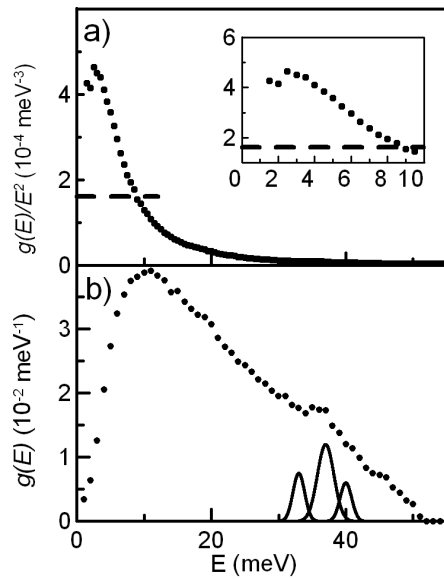


Figure 1. a) Reduced v-DOS $g(E)/E^2$ as a function of energy transfer E . (---) represents glucose v-DOS calculated in Debye approximation, as explained in the text. b) Generalized vibrational density of states measured with IN4 spectrometer as a function of energy transfer, together with a part of the Raman Spectrum (—) from ref.[12].

Figure 2 shows the v-DOS of both dry and hydrated DNA obtained by the one-phonon approximation applied to the experimental dynamic structure factor in wide momentum-energy range available in this experiment. The v-DOS obtained by integration of the measured dynamic structure factor over all wavevector transfer is shown for comparison. In this case the absolute normalization cannot be trivially obtained. We assumed an effective cross section deduced as the mean cross section per nucleus. The resulting fitting mass value was the mean mass per proton, inside the molecule, taking into account for the chemical composition of the DNA, as from ref [14], which is about 30 atomic units.

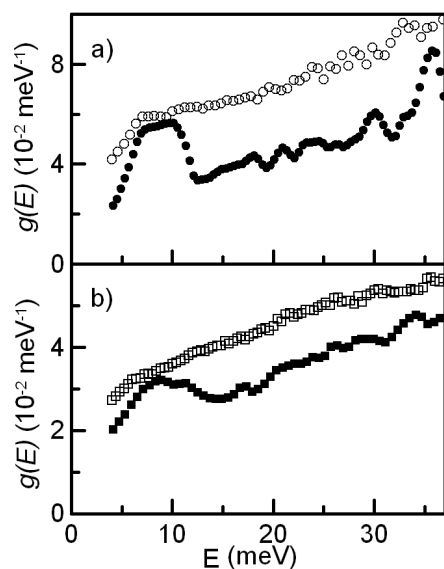


Figure 2. a) Density of states of hydrated (\bullet) DNA obtained by the one phonon approximation as stated in the text, compared to the integral of the measured dynamic structure factor on the wave vector transfer which are available in this experiment (\circ). b) Density of states of dry (\blacksquare) DNA is compared to the integral of the measured dynamic structure factor on the wave vector transfer which are available in this experiment (\square).

Figure 3 shows the v-DOS of the DNA hydration water, obtained by subtraction of the dry DNA spectrum from the hydrated one. It is compared to the $g(\omega)$ of pure bulk water taken from [15]. The comparison evidences the differences between the spectra due to the different temperatures

of the two measurements (100 K in the present experiment, 300 K in ref. [15] in the liquid phase). Indeed, the low temperature hydration water shows many sharp structures as it can be expected in this temperature range. The v-DOS of hydration water contains a considerable contribution from the phonon v-DOS of ice[16], which is also shown in Fig.3. This suggests a partial crystallization of the hydration water.

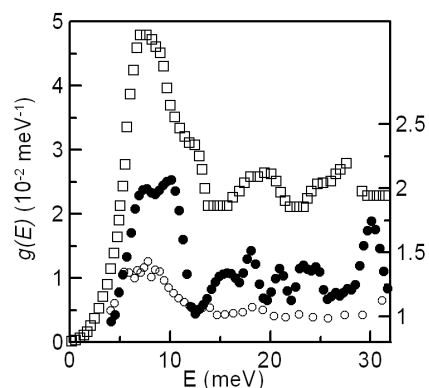


Figure 3. Density of states of three different systems: hydration water of DNA (●) as derived from the present data (see text), bulk liquid water (○) and solid ice (□) respectively from ref. [15] and [16]. Data are rescaled to be on the same scale. Data of bulk liquid water are shifted and referred to the scale on the right side.

4. Conclusions

The data treatment technique we presented was specifically developed to work out the vibrational density of states from neutron data. The advantage of this technique is the subtraction of multi-phonon contributions from the experimental dynamic structure factor by means of a self-consistent iterative procedure. Through this method we derived the one-phonon vibrational density of states of different disordered systems, by applying the incoherent approximation for isotropic systems to glassy glucose, and dry and hydrated DNA. The presented results are also discussed in comparison with available data for bulk water.

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