Complementarity of Thermal Restraint and RENS Approaches by Modeling Analysis

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Abstract

The aim of this contribution is to present complementary results obtained by Thermal Restraint (TR) and Resolution Elastic Neutron Scattering (RENS) approaches. More specifically, it is shown that the measured elastic scattering law as a function of temperature and of the logarithm of the instrumental energy of resolution give information on the system thermal response and on the system relaxation time. The RENS approach is tested numerically, taking into account a Gaussian resolution function and a Lorentzian scattering law, and experimentally by integrated EINS versus temperature (TR) and QENS measurements on three homologous disaccharide/water mixtures showing different relaxation times.

Keywords: Elastic Incoherent Neutron Scattering, Resolution Elastic Neutron Scattering, Quasi Elastic Incoherent Neutron Scattering, Thermal restraint, Disaccharides, Polymers, Proteins.

Introduction

The characterization of the molecular processes involved in condensed matter systems can be performed by Elastic Incoherent Neutron Scattering (EINS) by means of the so called "fixed-windows" method [1], where the scattered intensity is collected at $\omega = 0$ with a fixed "energy windows" corresponding to the instrumental energy resolution. This technique takes advantage from the fact that, besides to a relatively low number of fitting parameters, in respect to the quasi-elastic contribution at low energy transfer the elastic one is often a factor 100-1000 higher and then for obtaining good quality data in reasonable times, due to the usually limited neutron fluxes, one can cope with a relatively small amount samples, with small sized samples or with strongly absorbing samples.

The aim of this work is to present complementary results obtained by Thermal Restraint (TR) and Resolution Elastic Neutron Scattering (RENS) approaches, this latter being based on the acquisition of the measured elastic scattering law as a function of the instrumental energy resolution. In particular, the effect of the coupling between the system and the employed measuring instrument is considered and it is shown that the measured elastic scattering law as a function of the logarithm of the instrumental energy resolution behaves like an increasing sigmoid curve whose inflection point occurs when this the instrumental resolution time matches the system relaxation time. In order to test the validity of the approaches we shall consider three systems constituted by water mixtures of three homologous disaccharides, i.e. trehalose, maltose and sucrose and by two polymeric systems, i.e. Ethylene Glycol (EG) and Poly-Ethylene Glycol 400 (PEG 400); these systems are shown, by QENS measurements, to exhibit different dynamics as a function of temperature; as a consequence when tested by EINS measurements at a given instrumental energy resolution as a function of temperatures these systems are supposed to show, following the RENS approach, different inflection point temperatures. The collection of the measured elastic scattering intensity vs temperature, showing different inflection points for the three investigated systems, confirms the validity of the approaches. The measured elastic scattering law can be written as:

$$S_R = S(Q,\omega) \otimes R(Q,\omega)$$
$$= \frac{1}{\sqrt{2\pi}} \int_{+\infty}^{-\infty} I(Q,t) \cdot R(Q,t) e^{-i\omega t} dt. \quad (1)$$

In the ideal case of purely elastic scattering in which the resolution function is a delta in the -space, and hence a constant in the t-space, we obtain that being:

$$S_R(Q,\omega = 0) = \frac{1}{\sqrt{2\pi}} \int_{+\infty}^{-\infty} I(Q,t) \cdot R(Q,t) dt \quad (2)$$

the measured scattering law $S_R(Q,\omega)$ reduces to a time average of the intermediate scattering function $I(Q,t)$. A part from this ideal case, in the more general condition in which the resolution function in

the ω-space has a non negligible width, the experimentally measured elastic scattering law, due to the finite energy instrumental resolution $\Delta\omega$, $S_R^M(Q)$ is:

$$S_R^M(Q) = \int_{+\frac{\Delta\omega}{2}}^{-\frac{\Delta\omega}{2}} S_R(Q,\omega)d\omega \qquad (3)$$

and hence:

$$
\begin{aligned}
S_R^M &= \int_{-\frac{\Delta\omega}{2}}^{+\frac{\Delta\omega}{2}} S(Q,\omega) \otimes R(Q,\omega)d\omega \\
&= \int_{-\frac{\Delta\omega}{2}}^{+\frac{\Delta\omega}{2}} \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} I(Q,t) \cdot R(Q,t)e^{-i\omega t}dt \right] d\omega = \\
&= \int_{-\frac{\Delta\omega}{2}}^{+\frac{\Delta\omega}{2}} \left[\frac{1}{\sqrt{2\pi}} \int_{+\infty}^{-\infty} I(Q,t) \cdot R(Q,t)cos\omega t dt \right] d\omega.
\end{aligned}
$$
$$(4)$$

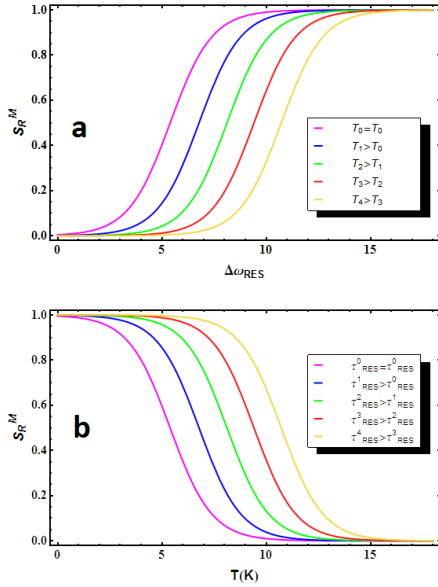being both the $S(Q,\omega)$ and R(Q,ω) functions even.

Figure 1: (a)Measured elastic scattering law, SRM, as a function of instrumental energy resolution for different temperature values.(b) Measured elastic scattering law, SRM, as a function of temperature for different instrumental resolution time values.

Figure 1 a shows the result the calculation of S_M^R as a function of the logarithm of the instrumental resolution. As it can be seen it shows an increasing sigmoid trend whose inflection point occurs when the linewidth of the resolution function approaches the linewidth of the system scattering law; in other words, in such a semi-logarithmic plot the inflection point occurs when the instrumental resolution time crosses the system relaxation time. Such a result shows the operating way of the RENS approach: from the inflection point of EINS profiles versus the logarithm of the energy resolution one can extract the

system relaxation time. It should be noticed that, in a complementary way, see fig. 1 b for a given fixed instrumental energy resolution function from EINS profiles versus temperature one is able to obtain from the inflection point the temperature value for which the system relaxation time equals the resolution time.
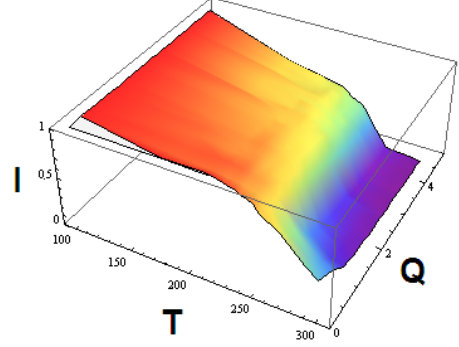
Figure 2: Elastic Incoherent Neutron Scattering intensity spectra, $S_M^R(Q)$, for EG as a function of temperature and wave-vector Q.
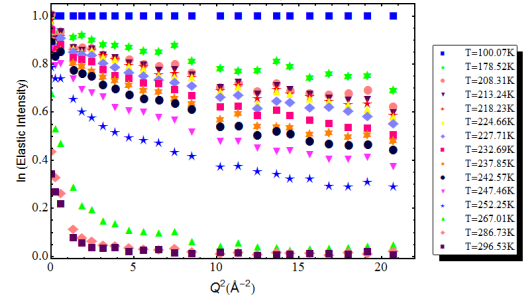
Figure 3: Elastically scattered intensity profile of EG as a function of the exchanged wavevector Q, in the range between 0.195 and 4.552 Å$^{(-1)}$, and at temperature values in the range from 100 K to 296 K. As it can be seen, by increasing temperature, the scattered intensity shows an almost linear trend at T=100 K and then, at the higher temperature values, it drops in Q.

Materials and Methods

Ultra pure trehalose, maltose and sucrose, EG, PEG 400, D_2O and H_2O, purchased by Aldrich-Chemie, were used for the experiment. EINS data were collected by the IN13 spectrometer at ILL (Grenoble, France). Quasi Elastic Neutron Scattering (QENS) measurements were performed in a temperature range of 283-320K on hydrogenated trehalose, maltose and sucrose ($C_{12}H_{22}O_{11}$) in H_2O and on partially deuterated trehalose, maltose and sucrose ($C_{12}H_{14}D_8O_{11}$) in D_2O at a weight fraction values corresponding to 19 water (H_2O and D_2O) molecules for each disaccharide molecule by the high resolution configuration of IRIS (graphite 002 and mica 006 analyser reflections) to measure sets of QENS

spectra covering a Q,ω-domain extending from $\hbar\omega$=-0.3 to 0.6meV (energy transfer) and Q=0.3 Å^{-1} to 1.8 Å^{-1} (momentum transfer) with a mean energy resolution of Γ=8μeV.

Result and discussion

In order to extract quantitative information from the $I(T)$ behaviors we performed a fit by using the following expression:

$$I(T) = A\left(1 - \frac{1}{1 + e^{B(T-T_0)}}\right) + (C - DT) \quad (5)$$

Here A represents the amplitude factor connected with the global thermal intensity behavior, whose inverse we call "thermal restraint"; it should be noticed that this quantity is not connected with a local behavior but represents a global property of the system. B is connected with the transition steepness, passing from smaller to higher values when the transition becomes more and more abrupt. As it can be inferred by following the RENS approach, T_0 is the inflection temperature, corresponding to the temperature value for which the system relaxation time equals the instrumental resolution time [4]. Finally, $C - DT$ represents the low temperature vibrational contribution. The analysis indicates a higher thermal restraint together with a higher transition temperature for trehalose in respect to the other two homologous disaccharides. Such a result confirms the validity of the RENS approach. In fact, taking into account the meaning of the transition temperature, the disaccharides-water relaxation times cross the resolution time at a different temperature values, i.e. 264 K for trehalose, 259 K for maltose and 257 K for sucrose.
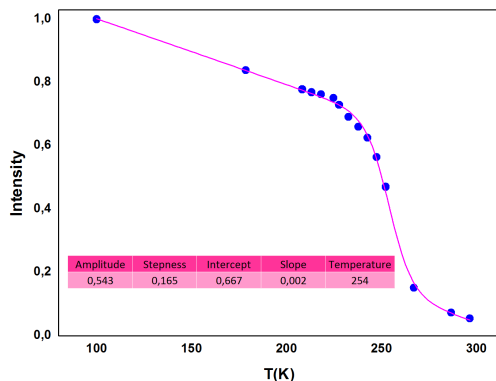

Figure 4: Intensity profile, obtained as sum for all the wavevector values, for EG versus temperature whose parameters of fitting are obtained taking into account eqn. (5). In the insert, the data fit parameters are reported.

The same approach has been applied for EG and PEG 400. In the insert of figure 4 the data fit parameters are reported for EG.

Conclusions

In conclusion, this contribution shows the operating approach of RENS from an analysis performed on the frequency space: from the inflection point of EINS profiles versus the logarithm of the energy resolution one can extract the system relaxation time. In a complementary way, for a given fixed instrumental energy resolution function from EINS profiles versus temperature one is able to obtain from the inflection point the temperature value for which the system relaxation time equals the resolution time.

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