

## Dynamic scaling of quasielastic neutron scattering spectra from interfacial water

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A method for analysis of high-resolution quasielastic neutron scattering (QENS) spectra of water in porous media is proposed and applied to the case of water in hydrated tricalcium and dicalcium silicates. We plot the normalized frequency-dependent susceptibility as a function of a scaling variable  $|\omega|/\omega_p$ , where  $\omega_p$  is the peak position of the susceptibility function. QENS data have been scaled into a single master curve and fitted with an empirical formula proposed by Bergman to obtain three independent parameters describing the relaxation dynamics of hydration water in calcium silicates.

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We have previously investigated the time evolution of translational dynamics of hydration water in a curing cement paste [1] using incoherent quasielastic neutron scattering (QENS). As a model system we used a cement paste made by mixing tricalcium silicate powder ( $C_3S$ ) with an appropriate amount of water. In order to study the kinetics of hydration reaction in the paste, time evolution of the QENS spectrum was followed every hour after the mixing of water, for a duration of about 40 h. We found that at 1 h after mixing, there is only a quasielastic component in the QENS spectrum. Interestingly, the QENS line shape is already distinctly non-Lorentzian, contrary to QENS line shape in bulk water at room temperature, which is known to be Lorentzian [2]. In other words, the relaxational dynamics of the center-of-mass translational motion of water molecules in the cement paste at room temperature is similar to the situation in supercooled bulk water, showing nonexponential behavior [3]. For this reason, we called the hydration water in cement as “glassy water.” As time goes by, an elastic component begins to develop in the QENS spectrum as well, showing that part of the glassy water is converted to bound water. Thus, the fraction of the glassy water shows an “age” dependence. In this paper, we present an alternative method for analysis of QENS data in two calcium silicates ( $C_2S$  and  $C_3S$ ), measured using a high-resolution disk chopper spectrometer (DCS) at the NIST Center for Neutron Research (NCNR). We analyze the susceptibility spectrum, defined as  $\chi''(Q, \omega) = \omega S_s(Q, \omega)$ , instead of the self-dynamic structure factor  $S_s(Q, \omega)$ . The normalized susceptibility can be plotted as a function of a scaling variable  $|\omega|/\omega_p$ , where  $\omega_p$  is the peak position of the susceptibility function. These dynamic scaling plots, for spectra taken in a range of  $Q$  (magnitude of the scattering vector), are shown to collapse into a single master curve, which can then be analyzed conveniently using an empirical formula proposed by Bergman [4]. As a result, we have a straightforward way of extracting the nonexponential relaxation parameters of the “glassy” water. We find the proposed method of analysis more intuitively appealing and simpler than the conventional one [1]. This method should find wide applications in diverse situations involving QENS studies of dynamics of hydration water in porous materials.

The hydrated paste was prepared by mixing 1 g of bidistilled water with 2 g of calcium silicate dry powder ( $C_2S$  or  $C_3S$ ) in order to obtain a 0.5 water/calcium silicate mass ratio. Samples were placed in a 0.5-mm-thick aluminum cell coated with teflon [1]. We followed the curing (aging) behavior of the cement paste at 25 °C by recording QENS spectra over a range of  $Q$  every hour for about 4 days. In the case of  $C_3S$  a 0.5% (in mass) retarder agent (sodium salt of sulfonated naphthalene-formaldehyde polycondensate, widely used in cement industry) was added to the paste to slow down the hydration process. The quasielastic neutron scattering experiments were carried out at NCNR, using the high-resolution DCS [5]. The incident monochromatic neutron wavelength was 9.0 Å (1.01 meV) which resulted in an energy resolution (full width at half maximum) of 20  $\mu$ eV. The sample cell was placed at 45° to the direction of the incident neutron beam. Only detectors in reflection geometry were taken into account. The detectors were grouped to obtain a set of five spectra in the  $Q$  range from 0.63 to 1.22 Å<sup>-1</sup>. The data were corrected for scattering from the same sample holder containing dry calcium silicate powder and standardized by dividing by the scattering intensity from a thin vanadium plate and converted to the double differential scattering cross section using standard routines available at NIST.

Since the incoherent scattering cross section of hydrogen is much larger than its coherent counterpart and also that of oxygen, the double differential scattering cross section in a quasielastic neutron scattering experiment on water is dominated by the term from the hydrogen self-dynamics. The self-dynamic structure factor [denoted by  $S_s(Q, \omega)$ , where  $Q = |\vec{k}_0 - \vec{k}| = (4\pi/\lambda)\sin(\theta/2)$  is the magnitude of the wave vector transfer,  $\hbar\omega = E_0 - E$  is the energy transfer,  $\vec{k}_0$  and  $E_0$  are the wave vector and energy of the incident neutrons,  $\vec{k}$  and  $E$  those of the scattered neutrons,  $\theta$  the scattering angle, and  $\lambda$  the incident neutron wavelength] has the property that its integral over all  $\omega$  is unity, and it is related to the intermediate scattering function (ISF),  $F_s(Q, t)$ , through a time Fourier transform. In our case, the ISF is composed of an elastic component, due to the presence of the immobile water

bound inside the colloidal particles, and a quasielastic component, coming from the glassy water embedded in amorphous gel regions surrounding the colloidal particles [1]. The ISF has thus been modeled as

$$F_s(Q, t) = p + q \{ F_v(Q, t) \exp[-(t/\tau)^\beta] \}, \quad (1)$$

where  $p$  is fraction of the immobile water,  $q = 1 - p$  fraction of glassy water,  $\tau$  the relaxation time, and  $\beta$  the stretched exponent. The relaxation function of the glassy water is given by the quantity contained in the curly brackets, according to the relaxing cage model developed by Chen *et al.* [6] for supercooled water.  $F_v(Q, t)$  takes into account the short time dynamics (up to about 0.2 ps) as vibrations of water molecules confined in a somewhat distorted, tetrahedrally coordinated, hydrogen bonded cage of its neighbors. It was shown that this dynamics, in the relevant energy range 0–40 meV, is describable by a proton density of states  $Z(\omega)$ , having a two peak structure: a prominent peak at  $\omega_1 = 8$  meV and a small peak at  $\omega_2 = 30$  meV.  $F_v(Q, t)$  decays to a plateau value (the Debye-Waller factor) given by

$$A(Q) = \exp \left\{ -Q^2 v_0^2 \left[ \frac{1-C}{\omega_1^2} + \frac{C}{\omega_2^2} \right] \right\} = \exp \left( -\frac{1}{3} Q^2 a^2 \right),$$

where  $v_0$  is the thermal speed of the particle (water molecule),  $C$  the relative strength of the two peaks in  $Z(\omega)$  and  $a$  represents the radius of the cage, which, from molecular dynamics simulations, has been found to be  $\sim 0.5 \text{ \AA}$  [7]. Thus, in the investigated  $Q$  range ( $0.63 - 1.22 \text{ \AA}^{-1}$ ),  $F_v(Q, t)$  is very nearly equal to unity and so is  $A(Q)$ . For times longer than 0.2 ps, the cage itself begins to relax, and water molecule can escape from it. Thus a trapped particle in the cage can migrate only through rearrangement of a large number of particles surrounding it. For this reason, there is a strong coupling between the particle motion and the density fluctuation of the fluid. In mode coupling theory, this process is called the  $\alpha$  relaxation and it is usually described by a stretched exponential function. This relaxing cage model was shown to fit QENS data on supercooled water in mesoporous glass matrices [3], and an extensive set of ISFs generated by computer molecular dynamics simulations of single point charge model supercooled water [6]. It was argued previously, with some experimental evidence, that the long-time dynamics of interfacial water behaves similarly to that of bulk supercooled water at a lower temperature [8]. According to the above sketched picture, the experimentally determined  $S_s(Q, \omega)$  should be analyzed by the following analytical function:

$$S_s(Q, \omega) = p \delta(\omega) + q A(Q) \mathcal{F} \{ \exp[-(t/\tau)^\beta] \}, \quad (2)$$

where  $\mathcal{F}$  is the Fourier transform. Since there is no analytical Fourier transform of the stretched exponential, the fitting procedure has to rely on numerical methods for calculating the Fourier integrals. This is a tedious task as the summation involves rapidly oscillating terms.

In order to avoid this problem we consider the susceptibility function  $\chi''(Q, \omega) = \omega S_s(Q, \omega)$ . This has the advantage

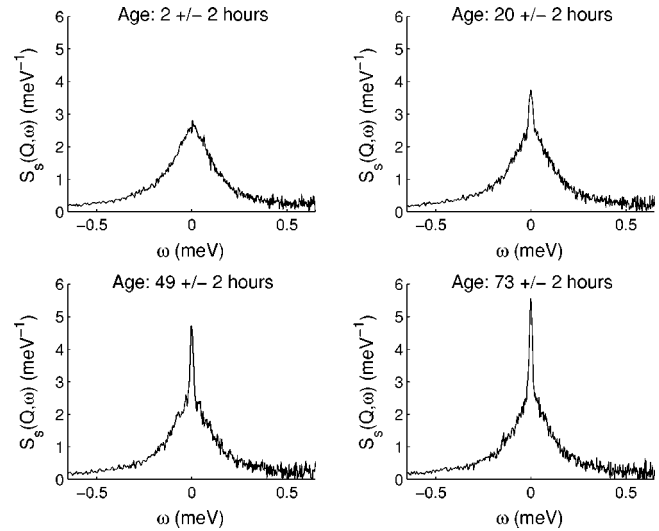


FIG. 1. Typical evolution of QENS spectra from the hydration water in the dicalcium silicate ( $C_2S$ ) sample at  $Q = 1.09 \pm 0.10 \text{ \AA}^{-1}$  and  $25 \text{ }^\circ\text{C}$ .

that it effectively removes the first term of the right-hand side of Eq. (2) so that for  $|\omega| > \omega_{resolution}$  the susceptibility is equal to:  $\chi''(Q, \omega) = q \omega \mathcal{F} \{ \exp[-(t/\tau)^\beta] \}$ . We can then represent the susceptibility (aside from a factor  $q$ ) using the recently derived empirical formula, [4]

$$\chi''(\omega) = \frac{\chi_p''}{1 - b + \frac{b}{1+b} [b(\omega_p/\omega) + (\omega/\omega_p)^b]}. \quad (3)$$

It has been reported that the above three-parameter equation is a good frequency domain representation of the susceptibility when the dynamic structure factor can be represented as the Fourier transform of a stretched exponential [4],  $\chi_p''$  and  $\omega_p$  are the height and position of the susceptibility peak, respectively, and the third parameter  $b$  determines the high  $Q$  asymptotic behavior of the curve, which is linear with a slope  $b$  in a log-log plot. It can be shown by numerical simulations that the parameters appearing in Eq. (3) can be identified with parameters in the stretched exponential relaxation function:  $b = \beta$  and  $\omega_p = [\tau \sqrt{\Gamma(1/b)/b}]^{-1}$ , where  $\Gamma$  is the  $\Gamma$  function. The height of the peak,  $\chi_p''$ , is then determined so that the  $\omega$  integral of  $\chi''(\omega)/\omega$  is unity, in order to satisfy the normalization property of the dynamic structure factor. Moreover, the fraction of glassy water in the cement paste,  $q = 1 - p$ , is proportional to the area of the quasielastic contribution. Since the spectra are normalized, it is given by the integral:  $q = 2 \int_0^\infty \chi''(\omega)/\omega d\omega$ .

Figure 1 shows some typical normalized QENS spectra for glassy water in  $C_2S$  at  $Q = 1.09 \pm 0.10 \text{ \AA}^{-1}$  as a function of aging. A few hours after mixing with water, the spectrum consists of only a quasielastic component as in the previous studies of  $C_3S$  pastes [1,9]. The line shape of this component is far from Lorentzian, showing that in the  $C_2S$  system, as in the  $C_3S$  system, the hydration water is confined in a microporous structured gel phase. The available experimental

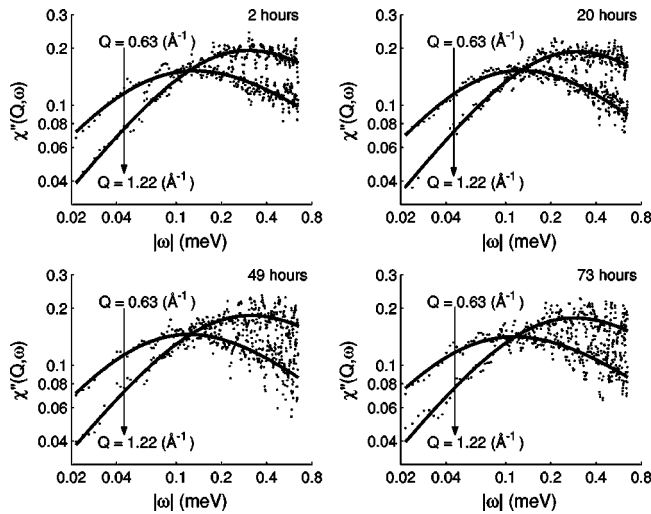


FIG. 2. Susceptibility of water in  $C_2S$  paste as a function of energy transfer and its  $Q$  dependence. Only the first and last  $Q$  values are shown for clarity. Continuous lines are the best fits according to Eq. (3).

data suggest that both the hydration mechanism and the C-S-H phase formed in the hydration process of  $C_2S$  are similar to that of  $C_3S$ . However, the hydration kinetics of pure  $C_2S$  is characterized by an extended induction period in which hydration is very slow, as compared to that of  $C_3S$ . Similarly to  $C_3S$ , this period is followed by a gradual increase of the hydration rate. In fact, as time passes, an elastic component appears and its intensity increases showing that the hydration reaction converts the glassy water contained in the calcium silicate hydrate (gel) into the bound crystalline water.

Figure 2 presents the susceptibility function obtained from the normalized QENS data in the energy transfer range from 0 to  $\pm 0.65$  meV. It is seen that the elastic part of the spectrum disappears in converting the dynamic structure factor to the susceptibility function. In the figure, only the lowest and highest  $Q$  data are shown. The value of  $Q$  mainly affects the peak position  $\omega_p$ . With increasing  $Q$  the peak position shifts to larger  $|\omega|$  and the peak becomes broader.

Normalizing each peak to the corresponding peak intensity  $\chi_p''$  and plotting the results as a function of the scaled energy transfer  $|\omega|/\omega_p$ , we obtain a master curve at each time (age) as shown in Fig. 3. This plot successfully scales out all the  $Q$  dependence of the spectra because the exponent  $b$ , which controls the large  $\omega$  asymptotic behavior, is only weakly dependent on  $Q$  in the investigated  $Q$  range. Fitting the curves in Fig. 3 with Eq. (3) and the definition of  $q$ , we obtain the parameters  $p$ ,  $\beta$ , and  $\bar{\tau} = 1/\omega_p$  shown by the symbols and solid lines in Fig. 4. As far as we know, these relaxation parameters for the  $C_2S$ /water system have been obtained experimentally for the first time here.

We would like to note at this point that this method of extracting the relaxation parameters has another advantage in that the analysis result is weakly dependent on energy resolution of the instrument used ( $20 \mu\text{eV}$ ), since the susceptibility peak is rather broad compared to the resolution function used to measure the quasielastic spectrum. In fact,

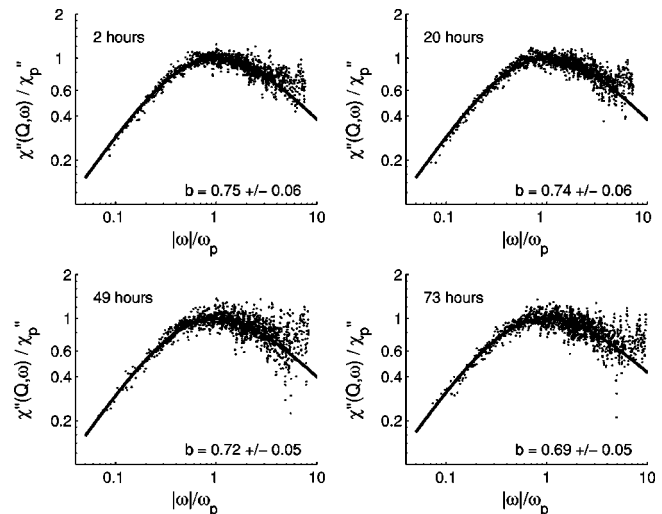


FIG. 3. Dynamic scaling plots of normalized susceptibilities of water in  $C_2S$  paste for five different  $Q$  values, at ages of 2, 20, 49, and 73 h. Continuous lines are the best fits according to Eq. (3).

we have also used the fitting function in which the  $S(Q, \omega)$  is first convolved with the resolution function before transforming into the susceptibility function and the resulting relaxation parameters obtained are identical.

In order to compare these parameters with the corresponding parameters in the  $C_3S$ /water case, which has been well studied before [1,9], we investigated the  $Q$  dependence of the QENS spectra obtained for a  $C_3S$  paste where the NSF retarder has been added. The advantage of the additive is to slow down considerably the aging process of the system, so effectively in the measurement time scale the spectra are invariant in time. We, therefore, take advantage of this fact by summing over all the data at each  $Q$  over the whole delay

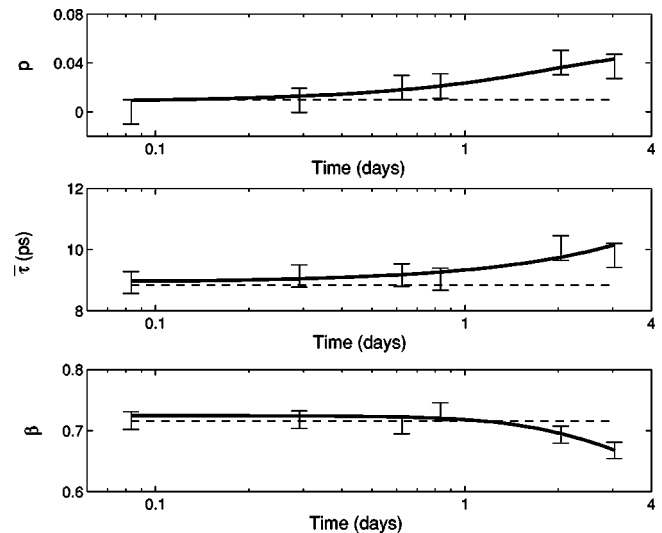


FIG. 4. Time evolution of the three parameters,  $p$ ,  $\bar{\tau}$ , and  $\beta$ , used to describe the aging behavior of water in curing  $C_2S$  (symbols and solid line) and  $C_3S$  (dash line) paste with the additive. While  $p$  and  $\beta$  are the averages over the investigated  $Q$  range, the value of  $\bar{\tau} = 1.09 \pm 0.10 \text{ \AA}^{-1}$  is reported in the second panel.

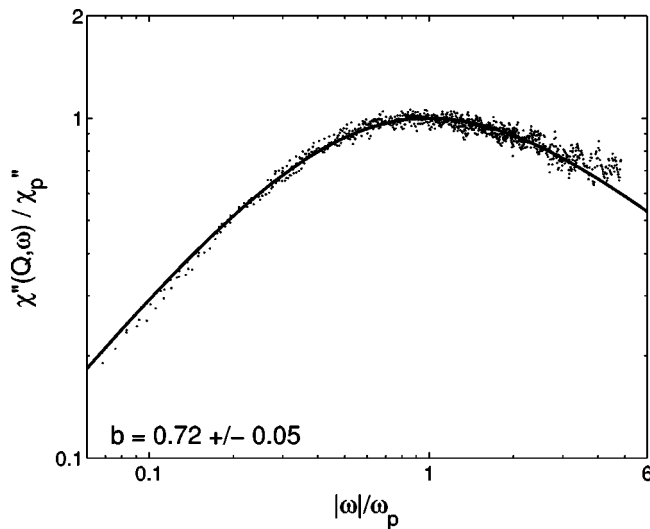


FIG. 5. Dynamic scaling plot of the normalized susceptibility for the five  $Q$  values, in the case of  $C_3S$  paste containing the additive. Continuous line is the best fit according to Eq. (3).

time (5 days) to improve the signal to noise ratio. As a result, we were able to produce the nice scaling plot shown in Fig. 5. The extracted parameters from this figure, by fitting the master curve with Eq. (3), are presented as dash lines in Fig. 4.

A nonexponential relaxation of the interfacial water at room temperature and at lower temperatures is a commonly

observed phenomenon. In this paper we have demonstrated the advantage of analyzing the susceptibility function in the frequency domain, instead of dealing with the dynamic structure factor directly. The reason is that Eq. (3) is an accurate representation of the susceptibility function when the ISF is a stretched exponential function [4]. In the  $Q$  range where  $\beta$  is approximately  $Q$  independent, the scaling plot as shown in Fig. 4, can be effectively used to extract the relaxation parameters of the interfacial water.

To the best of our knowledge, this is the first paper where the relaxation parameters,  $\beta$  and  $\bar{\tau}$ , of glassy water in  $C_2S$  and  $C_3S$  are compared. We found that they are of similar magnitude, indicating that pore structures of the gel phases in both the silicates are similar. Moreover, the hydration kinetics of the  $C_2S$ /water system is much slower than that of the  $C_3S$ /water system at the same temperature and in the absence of the additive [1], with the so-called induction period of about 20 h for the  $C_2S$ /water system (first panel of Fig. 4).

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