RAPID COMMUNICATIONS

PHYSICAL REVIEW E, VOLUME 65, 040501(R)

Rotational dynamics of hydration water in dicalcium silicate by quasielastic neutron scattering

A. Faraone,[1,2] S.-H. Chen,[1] E. Fratini,[1,3] P. Baglioni,[1,3] L. Liu,[1] and C. Brown[4]
[1]*Department of Nuclear Engineering, 24-209 MIT, Cambridge, Massachusetts 02139*
[2]*Department of Physics and INFM, University of Messina, Contrada Papardo, Salita Sperone 31, 98121 Messina, Italy*
[3]*Department of Chemistry and CSGI, University of Florence, via della Lastruccia 3-Sesto F.no, 50019 Florence, Italy*
[4]*Department of Material and Nuclear Engineering, University of Maryland, College Park, Maryland 207421 and NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 208991*

(Received 11 February 2002; published 8 April 2002)

Quasielastic neutron scattering (QENS) has been used to investigate the single-particle dynamics of interfacial water in dicalcium silicate (C_2S)/water paste. Our previous neutron-scattering studies on interfacial water have focused attention on the translational dynamics of the center of mass of water molecules. In this paper, we have collected QENS data on a wider range of wave-vector transfer so that both translational and rotational motions of water molecules are detected. The data have been analyzed by models for translation and rotation we recently proposed for supercooled water. The evolution of the parameters describing the relaxational dynamics of water embedded in the C_2S matrix is given at temperature $T = 303$ K as a function of the curing time.

DOI: 10.1103/PhysRevE.65.040501 PACS number(s): 61.20.Lc, 61.12.Ex, 64.70.Pf

Dynamics of interfacial water is a fundamental topic of condensed-matter research both because of its theoretical interest and because the study of the state of water near surfaces, or confined in nanopores, is relevant in many different applications, ranging from mining to biology. Hydration water in cement is an attractive example of this expanding field of research. Using quasielastic neutron scattering (QENS) we have already shown [1] that the translational dynamics of the center of mass of a water molecule can be described by the relaxing cage model [2] developed for supercooled water. Due to the confinement in the cage of its neighbors, the translational dynamics of a water molecule shows a short-time gaussian decay, followed by a long-time α relaxation [2]. We have recently extended this picture to include the rotational dynamics as well. Molecular-dynamics (MD) simulations of SPC/E water at low temperatures show that the rotational correlation functions exhibit a two-step relaxation, where the long-time decay is nonexponential, similar to that found for the translation [3]. In this paper, we shall apply this model for rotational dynamics to QENS data. Our experimental results confirm the validity of the model proposed, and allow us to get information on the rotational dynamics of water in a C_2S/water paste.

The reaction between the calcium silicates in Portland cement (PC) and water is the principal factor in the setting and hardening (curing or aging) of this popular building material [4]. Dicalcium silicate is one of the principal components of PC. The curing process has been exstensively investigated in the past using a number of experimental techniques, e.g., x-ray diffraction [5], differential scanning calorimetry [6], and more recently by QENS [1,7–9]. Hydrated cement paste contains calcium-silicate-hydrate in a gel form, generally denoted as C-S-H, and calcium hydroxide, $Ca(OH)_2$, abbreviated as C-H, in the form of colloidal particles imbedded in the C-S-H matrix. QENS experiments have shown that water molecules incorporated in the colloidal particles appear immobile on the QENS experimental time scale. On the other hand, water molecules dispersed in the C-S-H gel matrix behave as interfacial water, having a slow dynamics significantly different from that of bulk water at the same temperature. As cement ages, the interfacial water in C-S-H gel penetrates continuously into the colloidal particles and thus increases the immobile fraction [1,8].

QENS experiments were carried out at the National Institute of Standards and Technology (NIST) Center for Neutron Research using the Fermi chopper spectrometer. The incident neutron wavelength was chosen as $\lambda = 6.0$ Å or $E_0 = 2.2$ meV in energy. At this incident energy, the elastic energy resolution function has a Gaussian line shape with the full width at half maximum of about 66 μeV, as measured using a thin vanadium plate. The rectangular sample cell was placed at an angle making 45° from the direction of the incident neutron beam. The detectors facing the edge of the can have been discarded. The data have been grouped to obtain two sets of four and eight constant angle spectra, in transmission geometry, at low scattering angles, and in reflection geometry, at high scattering angles, respectively. The resulting wave-vector transfer range covered was $0.26\ \text{Å}^{-1} < Q < 1.94\ \text{Å}^{-1}$, at the elastic channel. The time-of-flight spectra were corrected for scattering from the same sample holder containing dry C_2S powder, standardized using the scattering data of the vanadium run, and converted to the differential scattering cross section by using standard routines available at NIST.

The investigated sample consisted of a paste with a 0.50 water/C_2S weight ratio, spread evenly on the can, making a layer of 0.5 mm, with an H_2O effective thickness of ~ 0.25 mm, so that multiple-scattering corrections were not necessary. Synthetic C_2S with BET specific surface area of 0.60 ± 0.05 m^2/g and particles median radius of 5.5 μm, has been used. The interior wall of the cans was coated with Teflon in order to prevent any interference of the aluminum in the hydration process of the cement. We collected data for about ten days in runs of three hours each. We confirm that successive runs superimpose with good accuracy and the data have been added in groups of four, resulting in spectra with a total of twelve hours of counting statistics.

Since the incoherent scattering cross section of hydrogen is much larger than its coherent counter part and also the total scattering of oxygen, silicon, or carbon the double-differential scattering cross section is dominated by the term from the hydrogen self dynamics. Thus, one measures essentially $S_H(Q,\omega)$, where $E=\hbar\omega$ is the energy transfer of the neutron to the system, and Q is the magnitude of the wave-vector transfer corrsponding to this energy transfer. The elastic Q value at a scattering angle θ is given by $Q_0=[4\pi\sin(\theta/2)]/\lambda$.

The self-dynamic structure factor is related to the hydrogen self-intermediate scattering function (ISF), $F_H(Q,t)$, through a time Fourier transform. In our case, ISF is composed of a constant part p representing the fraction of immobile water, and a relaxing function, coming from the structural relaxation of the interfacial water. The QENS data can then be analyzed using the following model for the dynamic structure factor [1]:

$$S_s(Q,\omega)=pR(Q_0,\omega)+(1-p)FT\{F_H(Q,t)R(Q_0,t)\} \tag{1}$$

where $R(Q_0,t)$ is the Fourier transform of the experimental resolution function, $R(Q_0,\omega)$.

The decoupling approximation for $F_H(Q,t)$ [10–12] is the working hypothesis most widely used to accurately model water dynamics. It assumes that $F_H(Q,t)$ is the product of the ISFs of the center of mass of the water molecule, $F_T(Q,t)$, and of the rotational ISF, $F_R(Q,t)$, of the hydrogen atom around the center of mass. This approximation has been tested against MD simulation data [12], and was confirmed that it is accurate to within ten percent, and suitable for the purpose of analyzing QENS data.

Our previous experiments on hydrated cement pastes investigated the $Q<1.2$ Å^{-1} range. Within this low-Q range, we need only to consider the translational dynamics, which can be described by the relaxing cage model [2]. In this model, the short-time translational dynamics of water confined in the cage of its neighbors is pictured as a harmonic vibration. For longer times, the cage itself begins to relax, and the molecule diffuses away. This process involves coupled motions of many molecules and is described by a stretched exponential function. Thus, the translational ISF of water is then given by the product of a short-time vibrational dynamics and a long-time cage relaxation

$$F_T(Q,t)=F_T^s(Q,t)\exp[-(t/\tau_T)^{\beta_T}] \tag{2}$$

where [2]

$$F_T^s(Q,t)=\exp\left\{-Q^2v_0^2\left[\frac{1-C}{\omega_1^2}(1-e^{-\omega_1^2t^2/2})+\frac{C}{\omega_2^2}(1-e^{-\omega_2^2t^2/2})\right]\right\}. \tag{3}$$

In the above equation, $v_0=\sqrt{k_BT/m}$ is the thermal speed of the water molecule, ω_1 and ω_2 the peak frequencies of the hydrogen atom translational density of states, $Z_T(\omega)$, and C their relative weight. The long-time dynamics is characterized by a structural relaxation time τ_T, and the average relaxation time $\overline{\tau_T}=\tau_T\cdot[\Gamma(1/\beta)]/\beta$, was shown to follow a power law in Q, namely, $\overline{\tau_T}=\overline{\tau_0}(aQ)^{-\gamma}$. a is the root-mean-square vibrational amplitude in the cage, defined by the Debye-Waller factor, which is the long-time limit of the $F_T^s(Q,t)$. According to MD simulations $a=0.5$ Å, and is fairly insensitive to temperature variation [2]. At moderate temperatures the exponent γ takes a value close to two, indicating a diffusional behavior [2,13,14]. On the other hand, our recent experimental results suggest that β_T is Q independent [1].

The Q and t dependence of the rotational ISF can be separated using the well-known Sears expansion [15]

$$F_R(Q,t)=\sum_{l=0}^{\infty}(2l+1)j_l^2(Qb)C_l(t), \tag{4}$$

where $C_l(t)$ is the lth order rotational correlation function. Since the center of mass to hydrogen atom distance in water is well known, $b=0.98$ Å, the Q dependence of the rotational ISF is fully determined. For Q range up to $Qb=2.5$ only four terms of this expansion are needed.

A model for the first-order rotational correlation function, $C_1(t)$ [3] has been proposed recently on the basis of MD simulation results. It applies the same picture developed for the translational dynamics in the relaxing cage model to the rotational dynamics: at short time, the water molecule is bound to its neighbors by H bonds, so that its reorientational dynamics are frozen, allowing only the harmonic angular vibrations around the H bond direction. At longer times, the H-bonds break and the water molecule can rotate and translate. Thus, $C_1(t)$ can be written as the product of a short-time gaussian part and an α-relaxationlike decay at long time

$$C_1(t)=C_1^s(t)\exp[-(t/\tau_R)^{\beta_R}]. \tag{5}$$

The short-time rotational dynamics is given by [3]

$$C_1^s(t)=\exp\left\{-\frac{4\langle\omega^2\rangle}{45\omega_3^2}\left[3\left(1-e^{\frac{-\omega_3^2t^2}{2}}\right)+6\omega_3^2t^2e^{\frac{-\omega_3^2t^2}{2}}-\omega_3^4t^4e^{\frac{-\omega_3^2t^2}{2}}\right]\right\}, \tag{6}$$

where $\langle\omega^2\rangle$ is the square average angular velocity, related to the effective moment of inertia of the water molecule in the cage and ω_3 the characteristic frequency of hindered rotations around the H-bond direction, known to be approximately 65 meV. The higher-order correlation functions are then generated from $C_1(t)$ using the maximum entropy method [16]. Equations (2)–(6) fully define the ISF in terms of 11 Q-independent parameters: p, C, ω_1, ω_2, τ_0, γ, β_T, $\langle\omega^2\rangle$, ω_3, τ_R, and β_R. Among them, four parameters, C, ω_1, ω_2, and ω_3 are known from MD data, through the com-

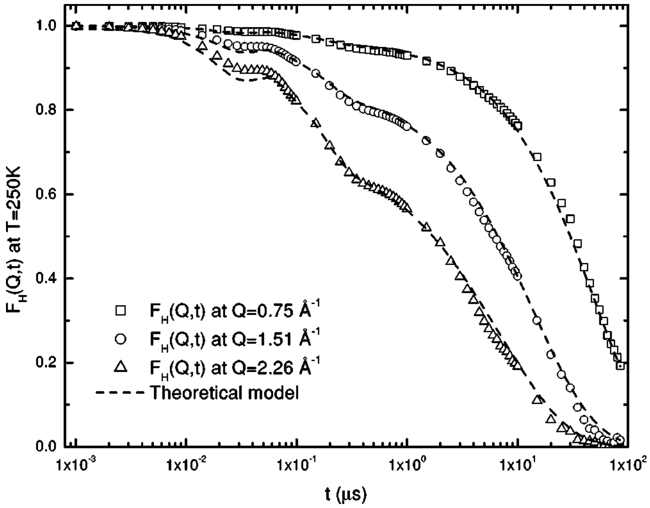

FIG. 1. Hydrogen self-intermediate scattering function from MD simulations on SPC/E water at $T=250$ K. Dashed lines represent the fit according to the model proposed in Ref. [3].

puted density of states of the hydrogen atom and are approximately temperature independent. The accuracy of the model has been tested against MD simulations on supercooled water. In Fig. 1, the comparison between the theory and MD result for $F_H(Q,t)$ is reported for three Q values at $T=250$ K, the temperature of maximum density for the SPC/E water. Our model is seen to be in excellent agreement with the MD data on ISF up to $t=100$ ps. This gives us confidence for the validity of this model for supercooled or intefacial water.

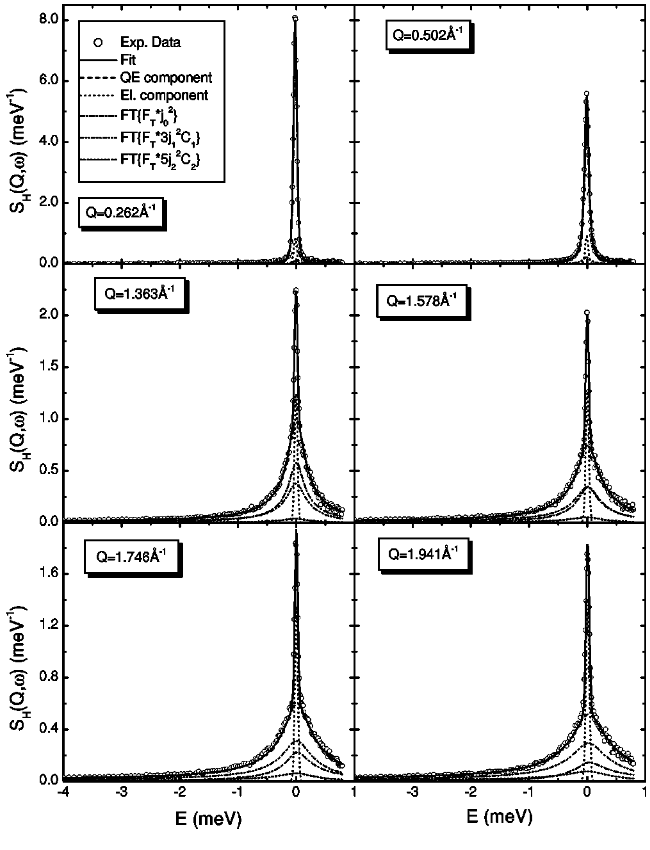

FIG. 2. Typical QENS spectra from hydration water in dicalcium silicate (C_2S) after ten days of aging time, at different Q values. The lines represent the result of the fitting procedure. The different components are shown as well.

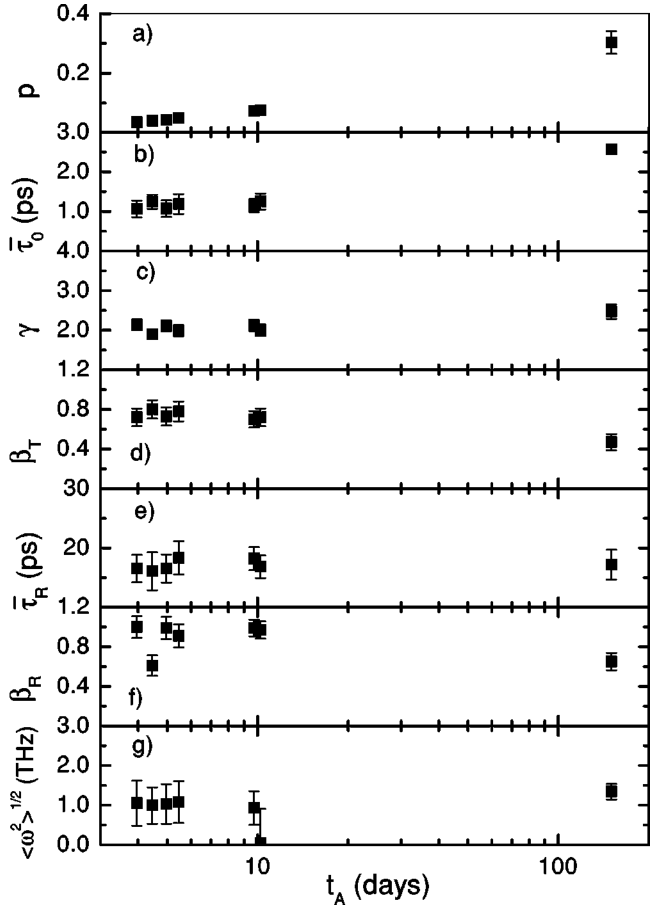

FIG. 3. Time evolution of the model parameters as obtained from the fitting procedure in curing C_2S/H_2O paste.

In this communication, the model has been used to analyze experimental data according to Eq. (1). The following seven parameters have been used as fitting variables: one parameter takes into account the fraction of immobile water, p; three are for the translational dynamics τ_0, γ, and β_T; and three for the rotational one $\langle\omega^2\rangle$, τ_R, and β_R. Since these parameters are Q independent, the twelve spectra have been fitted simultaneously using this model. The Q dependence of the energy-transfer E has been taken into account for every data point. Sears expansion has been truncated at the third term, since for $Qb<2$, three terms in the expansion are sufficent. The experimental data and the fitted results are reported in Fig. 2 for a C_2S/water paste aged for ten days as an example. The Q dependence of the line shape is evident, and clearly shows the relevance of the rotational dynamics on the high-angle spectra. Considering that the fitting parameters are Q independent, the quality of the fit is very good for all the spectra, giving further support to the validity of the model. In the figure, the elastic and quasielastic components (dashed and dotted lines, respectively) are shown. The dash-dotted, short-dash, and dash dotted-dotted lines are the three terms obtained by Fourier transform of the product of the translational ISF to the truncated Sears expansion. The rotational component is negligible at low Q values ($Q < 1$ Å^{-1}). However, it becomes more and more important for the high-angle spectra taken with the detectors in the reflection geometry.

The experiment has been performed on hydrated C_2S because this sample shows a slower aging behavior [9] allowing us to collect data for longer times, with better statistics. In the following, we show the aging dependence of the parameters describing the dynamics of the water molecules. In Figs. 3(b)–3(d), the translational parameters are reported. The characteristic relaxation time is constant in the first ten days, however it shows a noticeable increase over a longer period (five months). This behavior agrees with previous findings on the same sample that do not show any dependence of the translational dynamics over four days [9]. The exponent γ, being close to two, confirms the diffusional character of the translational dynamics. The values of β_T are in perfect agreement with the previous measurements and show a decrease after ten days. This finding has been already reported for the C_3S case [1] and has been connected to the fact that there is an increased confinement condition of water in the microporous structure of the gel phase as aging time increases. In Fig. 3(a) we report the values of p as a function of aging time. The parameter shows a slow increase for the first ten days, followed by a noticeable increase after five months. In the same figure (e)–(g), the relaxation parameters of the rotational dynamics are reported. They suggest that the rotational dynamics are not affected by the aging of the paste. The rotational relaxation time remains constant between 15 to 20 ps, about five times longer than the value in the bulk water measured at the same temperature [11]. As for β_R, it is constant initially, but decreases after five months. Theoretically $\langle \omega^2 \rangle = k_B T / I$, I being the moment of inertia of the water molecule in the cage, averaged over different axes. The experimental values are smaller than those expected for a free-water molecule. This finding indicates that, due to H bonding, the rotation of water is hindered, resulting in a higher effective moment of inertia.

In this communciation, we have analyzed QENS data taking into account both translational and rotational dynamics of water in a hydrated cement paste using a recently proposed model. The results of the translational dynamics are in agreement with previous findings. As far as rotations are concerned, the dynamics are not Debye-like, though very close to it at early aging time, but more and more ''stretched'' as the aging time increases. A quantitative average rotational relaxation time is given.

We are indebted to Dr. L. Cassar (Italcementi-CTG) for supplying pure samples of C_2S for this experiment. Research at MIT is supported by a grant from Materials Chemistry Program of US DOE Contract No. DE-FG02-90ER-45429. E.F. and P.B. acknowledge support from CSGI and MURST. They have enjoyed hospitality of the Nuclear Engineering Department of MIT while this work is being carried out. Finally, we are grateful to the Center for Neutron Research (NIST) for allocating neutron beam time at FCS.

---

[1] E. Fratini, S.-H. Chen, P. Baglioni, and M.-C. Bellissent-Funel, Phys. Rev. E **64**, 020201(R) (2001).

[2] S.-H. Chen, C. Liao, F. Sciortino, P. Gallo, and P. Tartaglia, Phys. Rev. E **59**, 6708 (1999).

[3] L. Liu, A. Faraone, and S.-H. Chen, Phys. Rev. E **65**, 041506 (2002).

[4] H. W. F. Taylor, *Cement Chemistry* (Academic Press, London, 1990).

[5] S. Brunauer, L. E. Copeland, and R. H. Bragg, J. Phys. Chem. **60**, 116 (1956).

[6] M. Moukwa, S. Farrington, and D. Youn, Thermochim. Acta **195**, 231 (1992).

[7] S. A. FitzGerald, D. A. Neumann, J. J. Rush, D. P. Bentz, and R. A. Livingston, Chem. Mater. **10**, 397 (1998).

[8] E. Fratini, S.-H. Chen, P. Baglioni, and M.-C. Bellissent-Funel, J. Phys. Chem. B **106**, 158 (2002).

[9] E. Fratini, S.-H. Chen, P. Baglioni, J. C. Cook, and J. R. D. Copley, Phys. Rev. E **65**, 010201(R) (2002).

[10] P. A. Egelstaff, *Thermal Neutron Scattering* (Academic Press, New York, 1971).

[11] J. Teixeira, M.-C. Bellissent-Funel, S.-H. Chen, and A. J. Dianoux, Phys. Rev. A **31**, 1913 (1985).

[12] S.-H. Chen, P. Gallo, F. Sciortino, and P. Tartaglia, Phys. Rev. E **56**, 4231 (1997).

[13] J.-M. Zanotti, M.-C. Bellissent-Funel, and S.-H. Chen, Phys. Rev. E **59**, 3084 (1999).

[14] V. Crupi, D. Majolino, P. Migliardo, and V. Venuti, J. Phys. Chem. A **104**, 11 000 (2000).

[15] V. F. Sears, Can. J. Phys. **45**, 237 (1967).

[16] B. J. Berne, P. Pechukas, and G. D. Harp, J. Chem. Phys. **49**, 3125 (1968).