Dynamic behaviors of water contained in calcium–silicate–hydrate gel at different temperatures studied by quasi-elastic neutron scattering spectroscopy

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The dynamic behaviors of water contained in calcium–silicate–hydrate (C–S–H) gel with different water content values from 10% to 30% (by weight), are studied by using an empirical diffusion model (EDM) to analyze the experimental data of quasi-elastic neutron scattering (QENS) spectra at measured temperatures ranging from 230 K to 280 K. In the study, the experimental QENS spectra with the whole Q-range are considered. Several important parameters including the bound/immobile water elastic coefficient A, the bound water index BWI, the Lorentzian with a half-width at half-maximum (HWHM) $\Gamma_1(Q)$ and $\Gamma_2(Q)$, the self-diffusion coefficients D_{t1} and D_{t2} of water molecules, the average residence times τ_{01} and τ_{02}, and the proton mean squared displacement (MSD) $\langle u^2 \rangle$ are obtained. The results show that the QENS spectra can be fitted very well not only for small $Q(\leq 1\ \text{Å}^{-1})$ but also for large Q. The bound/immobile water fraction in a C–S–H gel sample can be shown by the fitted BWI. The distinction between bound/immobile and mobile water, which includes confined water and ultra-confined water, can be seen by the fitted MSD. All the MSD tend to be the smallest value below 0.25 Å^2 (the MSD of bound/immobile water) as the Q increases to 1.9 Å^{-1}, no matter what the temperature and water content are. Furthermore, by the abrupt changes of the fitted values of D_{t1}, τ_{01}, and $\Gamma_1(Q)$, a crossover temperature at 250 K, namely the liquid-to-crystal-like transition temperature, can be identified for confined water in large gel pores (LGPs) and/or small gel pores (SGPs) contained in the C–S–H gel sample with 30% water content.

Keywords: dynamics of water, quasi-elastic neutron scattering spectra, empirical diffusion model, C–S–H gel pastes

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1. Introduction

Water is the most abundant compound on the Earth's surface, and also the most important component in organisms. The properties of water on a nanoscale are quite different from those in large volume.[1–4] Both bound/immobile water and water molecules confined in micro-nano pores exist in calcium–silicate–hydrate (C–S–H) gel, which is the main component of aged Portland cement pastes. The dynamic behaviors of these water molecules influence the durability and mechanical properties of aged cements, which are the most commonly used construction materials in our society. It is known that quasi-elastic neutron scattering (QENS) spectroscopy,[5–7] differential scanning calorimetry (DSC),[8,9] nuclear magnetic resonance (NMR) spectroscopy,[10,11] and dielectric spectroscopy (DS)[12,13] are experimental methods to investigate the dynamic behaviors of water contained in pores of C–S–H gel and cement pastes. QENS is one of the best options to study the dynamic behaviors of water confined in gel pores existing in C–S–H gel samples, because the interaction cross section of hydrogen atoms with neutrons is much larger than that of other constitutive atoms contained in C–S–H gel.

C–S–H is a gel-like material,[14–16] and there are several models to describe it.[17–20] The Jennings's colloidal model-II (CM-II) is a commonly accepted C–S–H structural model,[19,20] in which the layered C–S–H is saturated with water to form a nanoscale object, a "globule", and the globules clusterize into fractal objects with an associated pore system. According to the CM-II,[20] the pore structure in C–S–H gel has been described and categorized in detail. There are mainly three types of nanoscale gel pores. One is an interlayer gel pore (IGP) which is the very small cavity existing between C–S–H layers with a size of smaller than 1 nm. Another two are formed by packing C–S–H globules identified as the small gel pores (SGPs) with sizes of 1 nm–3 nm, and the large gel pores (LGPs) with sizes of 3 nm–12 nm. In a C–S–H gel, confined water molecules mainly exist in the SGPs and LGPs, and a smaller amount of water is present in the IGPs.[21]

To the best of our knowledge, there are mainly three types of models for fitting QENS spectral data from C–S–H gel and cement paste samples, which are the empirical diffusion model (EDM),[5,22] the relaxing cage model (RCM),[23] and the jump–diffusion and rotation–diffusion model (JRM).[6,24] In our previous study,[7] the dynamical behavior of hydration water in C–S–H gel samples with different water contents and at different measured temperatures were investigated by QENS experiments. The fitting model used was RCM in which the QENS spectral data analyzed were limited only in

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the $Q \leq 1$ Å^{-1}. In the present work, we adopt the EDM to fit the same QENS spectra, thus the whole Q range can be analyzed, not only for $Q \leq 1$ Å^{-1} but also for $Q > 1$ Å^{-1}. The results indicate that all the QENS spectra are fitted very well. The contributions from the elastic part, due to bound/immobile water, and the quasi-elastic part, due to confined and ultra-confined water, are clearly separated. By the non-linear least square fitting of the normalized QENS spectra, several important parameters describing the dynamics of water in the C–S–H gel samples are extracted. These fitted parameters include the bound/immobile water elastic coefficient A, the bound water index BWI, the Lorentzian with a half-width at half-maximum (HWHM) values $\Gamma_1(Q)$ and $\Gamma_2(Q)$, the self-diffusion coefficients D_{t1} and D_{t2} of water molecules, the average residence times τ_{01} and τ_{02}, and the proton mean squared displacement (MSD) $\langle u^2 \rangle$. Compared with those of molecular dynamics simulation,[25] the fitted values of MSD can be attributed to the bound/immobile and the mobile water, which includes confined and ultra-confined water. When Q is small, the larger MSD corresponds to the confined water in the LGPs and/or SGPs. As Q increases, the MSD gradually decreases, corresponding to the ultra-confined water in the IGPs. As Q increases continually, the MSD tends to be the same smallest value for all the C–S–H gel samples, no matter what the water content and the measured temperature are. This shows that the smallest MSD can be attributed to the bound/immobile water. Moreover, from these fitted parameters, we can see that the values of D_{t1}, τ_{01} and $\Gamma_1(Q)$ change abruptly at temperature 250 K only for the C–S–H gel sample in the case of 30%. This shows that there exists a crossover temperature at 250 K, probably a liquid-to-crystal-like transition temperature, for water confined in the C–S–H gel. The above two features are most considered and discussed in this paper.

2. Fitting of QENS spectra

QENS spectral data analyzed here are from C–S–H gel samples investigated by a QENS experiment done before.[7] These QENS data are acquired by using the high-resolution backscattering spectrometer BASIS[26] at the Oak Ridge National Laboratory (ORNL) Spallation Neutron Source (SNS). The spectrometer has an energy resolution of 3.5 μeV. The dynamic range of neutron energy is chosen to be ±120 μeV, which allows the dynamic behaviors of water molecules to be measured in a time range from 10 ps to 1 ns. The QENS spectra are measured by 9 detectors, where the scattering vector Q values are in a range of 0.3 Å^{-1}–1.9 Å^{-1}.

In the QENS experiment, three C–S–H gel samples with different water content values and an empty cell holder were measured at different temperatures ranging from 230 K to 280 K. The resolution function $R(Q,E)$ is measured at 3.5 K for each C–S–H gel sample. Synthetic C–S–H is prepared by hydrating pure tricalcium silicate (C_3S) in an excess of decarbonated water. The synthesis is conducted at 25±2 °C. The resulting gel is dried to the desired water content by using a vacuum oven operating under an N_2 atmosphere at temperatures below 100 °C. Water content values of 10%, 17%, and 30% (weight percent=grams of water divided by grams of dry cement) are achieved at the end.[7] Table 1 gives a list of all the measured C–S–H gel samples with different water content values and the measured temperatures.

Table 1. List of the C–S–H gel samples with different water content measured at different temperatures.

Samples with water content (by weight)	Measured temperatures/K
10%	280, 270, 260, 250, 240, 230
17%	280, 270, 260, 250, 240
30%	280, 270, 260, 250, 240, 230

In order to have smooth resolution function in data analysis, while minimizing the errors introduced during the convolution operation, the measured resolution function $R(Q,E)$ is fitted by a sum of four Gaussian functions[27,28] for each C–S–H gel sample at each Q:

$$R(Q,E) = \sum_{i=1}^{4} \frac{F_i}{\sqrt{2\pi}\sigma_i} \exp\left[-\frac{(E-E_i)^2}{2\sigma_i^2}\right], \qquad (1)$$

where Q is the magnitude of the wave vector transfer of scattered neutrons, E the neutron energy transfer, F_i the amplitude, E_i the peak position, and σ_i the width of each Gaussian component. Twelve parameters including F_i, E_i, and σ_i ($i = 1$, 2, 3, and 4) are obtained by the fitting, and the smooth $R(Q,E)$ is obtained from Eq. (1).

Figure 1 shows the measured resolution function fitted by a sum of four Gaussians for the C–S–H gel sample with 30% water content at $Q = 0.5$ Å^{-1} and 1.5 Å^{-1}. The upper two panels show the measured values and the fitted curves, and the lower two display the corresponding normalized $R(Q,E)$spectral data and fitted curves. It can be clearly seen that the measured $R(Q,E)$ can be fitted very well by four Gaussians for both $Q \leq 1$ Å^{-1} and $Q > 1$ Å^{-1}. In this way, a smoother $R(Q,E)$ can be obtained from the measured $R(Q,E)$ for each C–S–H gel sample at each Q.

QENS spectra can provide information about the dynamics of water contained in C–S–H gel. EDM is one of the used models to fit QENS data and has already been used extensively.[5,22,28,29] The physical meaning of EDM and the reason why it is suitable for the whole Q range can be explained in the following. This is mainly because the movement of a water molecule includes its translational and rotational motions. These two motions can be assumed to be non-correlated, resulting in the convolution of the scattering laws and the obtainment of Eq. (1) in Ref. [24]. The translational component

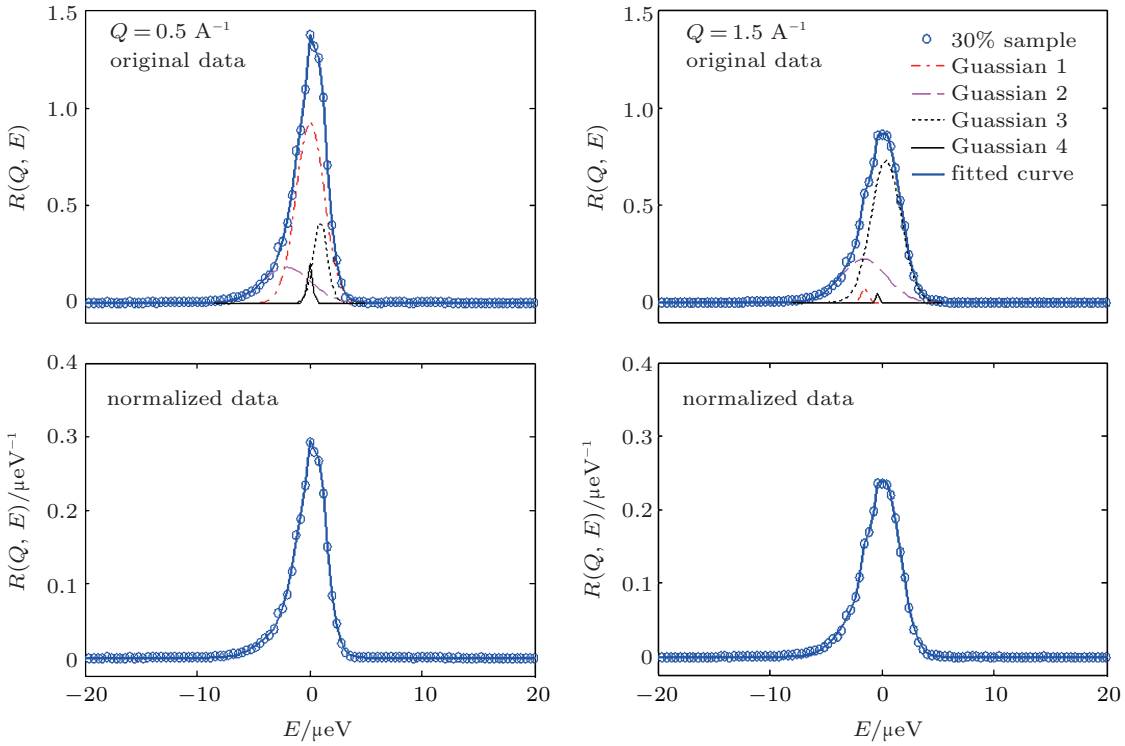


Fig. 1. (color online) Resolution function of the C–S–H gel sample with 30% water content at Q values of 0.5 Å^{-1} and 1.5 Å^{-1}. The upper two panels show the measured resolution functions fitted by four Gaussian functions, while the lower two display the curves corresponding normalized $R(Q,E)$.

is usually modeled by a Lorentzian, and the rotational motion is expressed by the Sears expansion. Taking two terms ($l = 0$ and 1) in Sears expansion, the EDM of Eq. (2) used here can be obtained. By the EDM, the measured neutron intensity $S_{\rm inc}(Q,E)$ as a function of energy transfer E at each Q can be decomposed into three parts. One is a Gaussian term representing an elastic neutron scattering (ENS) coming from immobile water contained in C–S–H gel. The other two are Lorentzian terms representing QENS broadening coming from the confined water molecules, and the ultra-confined water molecules, respectively. The EDM can be expressed as follows:[5]

$$S_{\rm inc}(Q,E) = \left\{A\delta(E) + B_1\left[\frac{\Gamma_1(Q)}{\pi(\Gamma_1(Q)^2+E^2)}\right] + B_2\left[\frac{\Gamma_2(Q)}{\pi(\Gamma_2(Q)^2+E^2)}\right]\right\} \otimes R(Q,E), \quad (2)$$

where $S_{\rm inc}(Q,E)$ is the incoherent scattering intensity; $\delta(E)$ is the Dirac delta function; parameters A, B_1, and B_2 are the coefficients corresponding to bound/immobile water, confined water, and ultra-confined water, respectively; $\Gamma_1(Q)$ and $\Gamma_2(Q)$ are the Lorentzian with a half-width at half-maximum (HWHM) attributed to confined water and ultra-confined water, respectively.

According to the model by Singwi and Sjölander,[30] the Q-dependence HWHM can be given by

$$\Gamma(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0}, \quad (3)$$

where D_t is the self-diffusion coefficient of water molecules, and τ_0 the average residence time. By using $\Gamma_1(Q)$ and $\Gamma_2(Q)$ in Eq. (3) respectively, we can obtain the self-diffusion coefficients D_{t1} of confined water and D_{t2} of ultra-confined water, and the corresponding average residence times τ_{01} and τ_{02}.

Furthermore, the bound water index (BWI) can be obtained with the coefficients A, B_1, and B_2 from the following expression:[5]

$$\text{BWI} = \frac{A + B_2}{A + B_1 + B_2}. \quad (4)$$

Since the coefficient A is also the bound/immobile water elastic coefficient, namely the Debye–Waller factor,[7,24,28] we have

$$A = C * \exp(-\langle u^2 \rangle Q^2), \quad (5)$$

where C is a constant for a measured temperature and $\langle u^2 \rangle$ denotes the mean squared displacement (MSD) of the proton in a water molecule.

3. Results

By using the EDM, the measured QENS spectra from the C–S–H gel samples (listed in Table 1) can be fitted very well for the whole Q range. Firstly, five parameters, i.e., A, B_1, B_2, $\Gamma_1(Q)$ and $\Gamma_2(Q)$ are extracted by fitting the incoherent scattering intensity $S_{\rm inc}(Q,E)$ with Eqs. (1) and (2) for each Q value. Then, parameters of D_{t1} and τ_{01}, or D_{t2} and τ_{02}, can be obtained by replacing the part on the right-hand side of Eq. (3) by the fitted $\Gamma_1(Q)$ or $\Gamma_2(Q)$. Further, the BWI and MSD can be calculated by Eqs. (4) and (5), respectively. Here,

the flat background has already been subtracted, and the intensity $S_{\rm inc}(Q,E)$ and the fitted resolution function $R(Q,E)$ have been normalized to unity before the QENS spectra fitting.

Figure 2 shows the fitted results of the measured QENS spectra from the C–S–H gel sample with 30% water content for $Q = 0.5$ Å^{-1} and 1.5 Å^{-1} at measured temperature 250 K. The measured QENS data (blue empty circle), the ENS component (red dash dotted line), the single Lorentzian terms QENS_S (black dash line) or the two Lorentzian terms QENS1 (black dash line) and QENS2 (black dotted line), and the fitted curve (blue solid line) are all shown in Fig. 2. To show the better fitting by two Lorentzian functions, the upper two panels in Fig. 2 show the single Lorentzian function fitting first. It can be clearly seen that the single Lorentzian function fitting is not good for $Q = 0.5$ Å^{-1} nor for $Q = 1.5$ Å^{-1}. This is because there are three kinds of water,[5] which are structural (bound) water, and liquid (confined) water, and loosely bound (ultra-confined) water. The single Lorentzian function is not enough to describe the QENS spectrum broadening due to the latter two kinds of water. From the lower two panels in Fig. 2, it can be seen that the QENS spectral fittings are quite good, and the QENS spectral broadening is separated into QENS1 and QENS2 by Eq. (2), which come from confined water and ultra-confined water, respectively. According to the Jennings's colloidal model-II,[20] the confined water is mainly in LGPs and SGPs contained in C–S–H gel, while the ultra-confined water in IGPs. So we can attribute the QENS1 to the confined water in LGPs and SGPs, and the QENS2 to the ultra-confined water in IGPs. Comparing the values of QENS1 and QENS2, it can be seen that the water confined in LGPs and SGPs is the main factor inducing QENS spectral broadening. Furthermore, from Fig. 2, it can be seen that both the peaks of QENS1 and QENS2 are narrower and higher for $Q = 0.5$ Å^{-1} than those for $Q = 1.5$ Å^{-1}. This is consistent with the result of HWHM shown in Fig. 5.

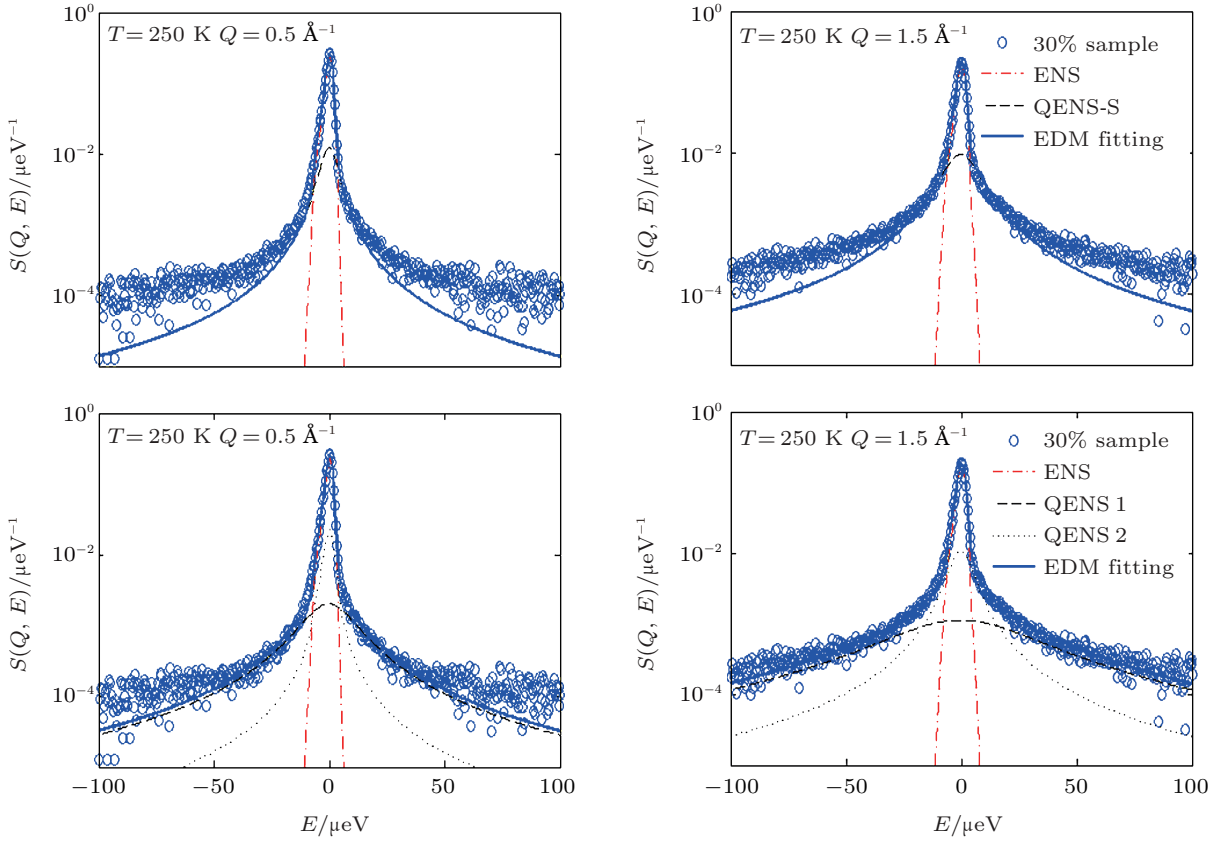


Fig. 2. (color online) QENS spectra from the C–S–H gel sample with 30% water content for $Q = 0.5$ Å^{-1} and 1.5 Å^{-1} at measured temperature 250 K. The upper two panels show the fitting by single Lorentzian function and the lower two panels by two Lorentzian functions.

Figure 3 shows the extracted six parameters fitted for the whole Q range: the bound/immobile water elastic coefficient A, the bound water index BWI, the self-diffusion coefficient D_{t1} of confined water and D_{t2} of ultra-confined water, and the corresponding average residence times τ_{01} and τ_{02}. Here, all the parameter values are averaged over Q for each measuring temperature. From Fig. 3(a), it can be clearly seen that the bound/immobile water elastic coefficient A decreases continuously with increasing the measured temperature and/or the water content of the C–S–H gel sample. Similar results can also be reached by observing the BWI in Fig. 3(b), showing that the ratio of immobile water in the samples decreases with increasing the measured temperature and/or the water content. This can be explained as that more water molecules are bound

in the C–S–H gel for lower measured temperature and/or water content level. From Figs. 3(c) and 3(d), we can see that D_{t1} and τ_{01} maintain almost the same values within error bars for the samples in the cases of 10% and 17%, as the measured temperature increases. However, D_{t1} increases and τ_{01} decreases as the measured temperature is higher than 250 K in the case of 30%. This indicates that self-diffusion coefficient D_{t1} of the confined water molecules and the average residence time τ_{01} are sensitive to temperature only for the 30% water level case. This conclusion is consistent with the result in our previous work.[7] From Figs. 3(e) and 3(f), we can see that D_{t2} and τ_{02} have the same change trends as the D_{t1} and τ_{01} for 10% and 17% samples, while D_{t2} increases and τ_{02} decreases continually as measured temperature increases for the 30% case. The reason will be explained in the Discussion section. Comparing the values of these parameters, we can also see that the D_{t2} is one order of magnitude smaller than D_{t1}, while the τ_{02} is larger than the τ_{01}. This shows that the water is more confined in IGPs than in SGPs and in LGPs. These results are new compared with those in our previous similar work.[7]

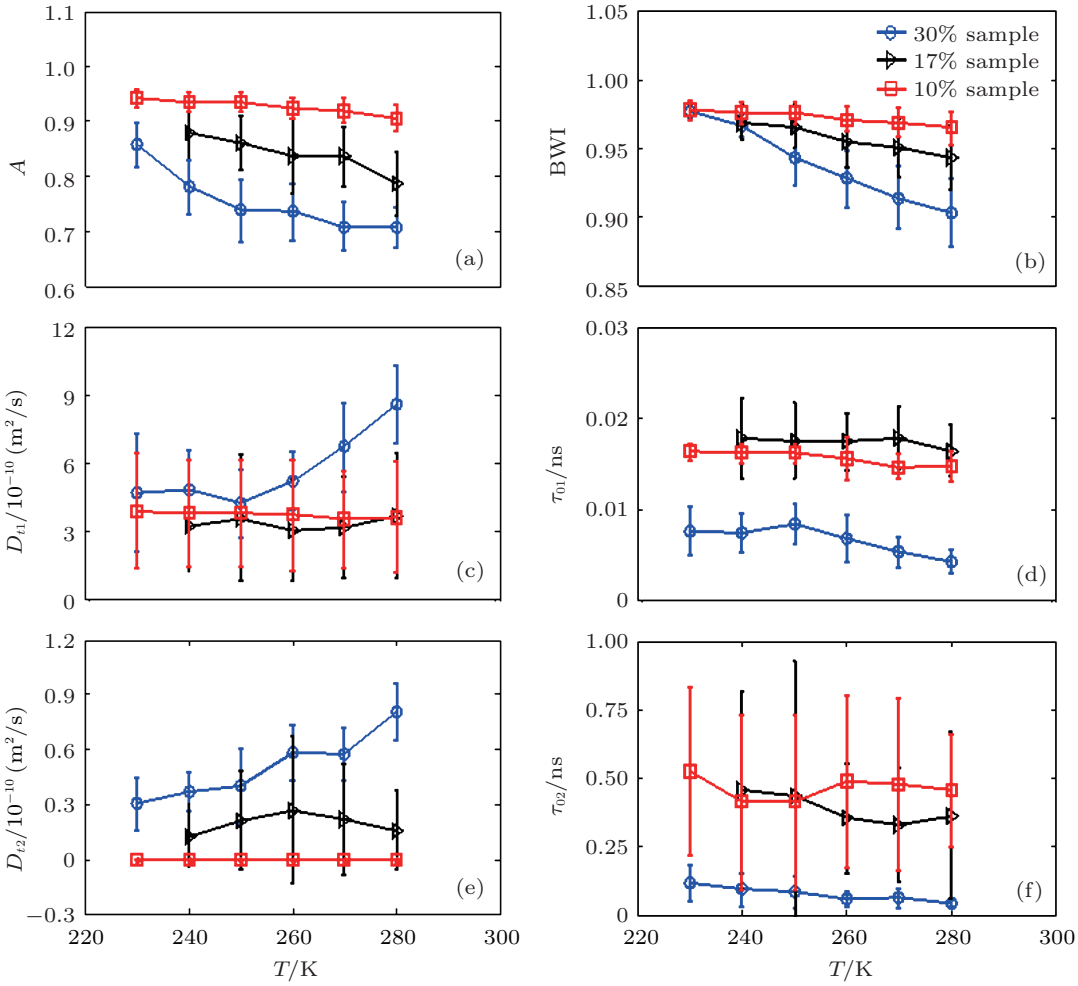


Fig. 3. (color online) Variations of extracted six parameters with temperature for all the C–S–H gel samples listed in Table 1: (a) bound/immobile water elastic coefficient A, (b) BWI, (c) self-diffusion coefficient D_{t1} of confined water molecules, (d) average residence time τ_{01}, (e) self-diffusion coefficient D_{t2} of ultra-confined water molecules, and (f) average residence time τ_{02}.

Figure 4 shows the Q-dependent MSDs of water contained in C–S–H gel samples with water content values of 30%, 17% , and 10% at measured temperatures from 230 K to 280 K, where the inset shows temperature profile versus Q. From Figs. 4(a) to 4(c), we can see that the fitted values of MSD decrease with increasing Q for all the water content values and the measured temperatures. This can be explained as follows. It is already known that the water contained in C–S–H gel samples can be divided into bound/immobile water, confined water, and ultra-confined water. The confined and the ultra-confined exist mainly in three kinds of nanometer gel pores according to Jenning's colloidal model-II,[20] which are LGPs, SGPs, and IGPs. When Q is smaller, the larger MSD belongs to the confined water in the LGPs and SGPs, where the pore size is larger than 1 nm. As Q increases, the value of MSD gradually decreases. The smaller MSD belongs to the ultra-confined water in the IGPs, where the pore size is smaller than 1 nm. As the Q increases continually, the MSD tends to be the same smallest values for all the C–S–H gel samples, no matter what the water content and the measured temperature are. This denotes that the smallest MSD belongs to the bound/immobile water. The above results are consis-

tent with those of the fitted MSD of Portland cement paste samples in our previous work[24] and the molecular dynamics simulations.[25] Moreover, from Figs. 4(a) to 4(c), for the same measured temperature, it can be seen that the values of MSD increase with increasing the water content when Q is small, while it tends to be the same values (< 0.25 Å^2) as Q is large. This can be explained as that more water molecules exist as confined water molecules in LGPs and SGPs in the case of 30%, while most water molecules mainly exist as ultra-confined water molecules in IGPs or as bound/immobile water molecules in the cases of 17% and 10%.

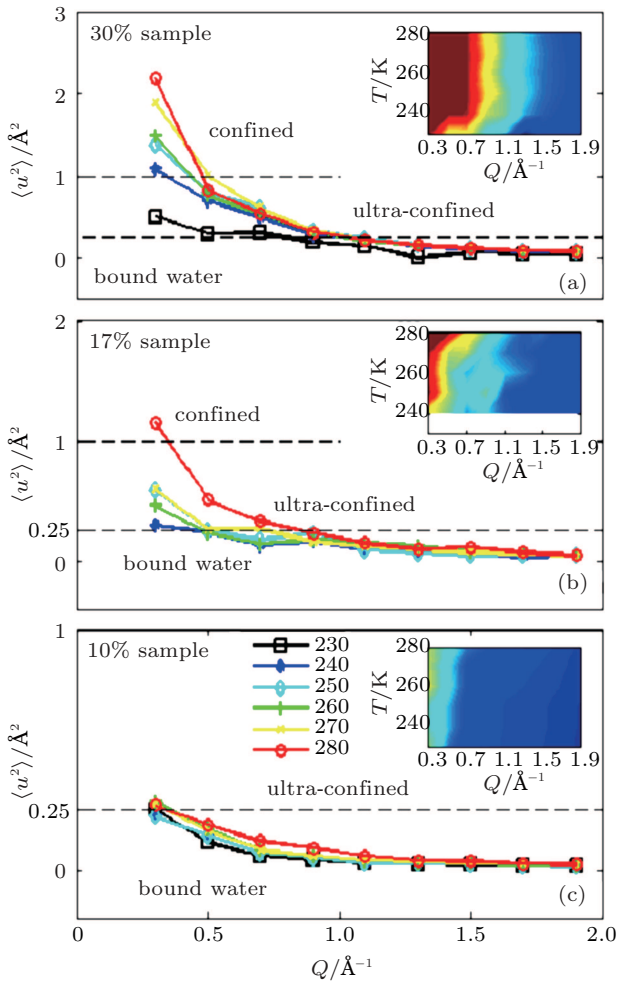


Fig. 4. (color online) Fitted MSDs of water contained in the C–S–H gel samples with water content values of (a) 30%, (b) 17%, and (c) 10 % at the measured temperatures from 230 K to 280 K. The inset displays the Q-dependent temperature profile.

Based on values of the fitted MSD, the averaged values of MSD can be obtained to be in a range of 0.1 Å^2–0.5 Å^2 for all the C–S–H gel samples shown in Table 1. These values are smaller than 0.4 Å^2–1.2 Å^2 shown in Fig. 3(d) in our previous work.[7] This is reasonable because the larger averaged MSD in our previous work was obtained only for small $Q \leq 1$ Å^{-1}, which represents the MSDs of confined and ultra-confined water in LGPs, SGPs, and IGPs, not including that of bound/immobile water. The smaller averaged MSD here in this work is obtained for the whole Q range, which includes not only those of confined and ultra-confined water but also those of bound/immobile water.

4. Discussion

Regarding the fitted parameters of D_{t1}, D_{t2}, τ_{01}, and τ_{02}, we can see that these parameters are sensitive to the measured temperature only for the C–S–H gel sample with 30% water level (see Figs. 3(c)– 3(f)). To see more clearly, the left two panels in Fig. 5 show these four parameters only for the case of 30%, in which D_{t1} and τ_{01} describe the water confined in LGPs and SGPs, while D_{t2} and τ_{02} the water ultra-confined in IGPs. From Figs. 5(a) and 5(c), it can be clearly seen that there are changes of the behaviors for both D_{t1} and τ_{01} at temperature 250 K, but not for D_{t2} nor τ_{02}. This means that the water confined in LGPs and/or SGPs at below and above temperature 250 K exhibit different dynamic behaviors, while the water ultra-confined in IGPs does not and remains amorphous. A similar behavior at 250 K has also been reported in the relevant experimental results.[8,9,31,32] All this shows that the 250 K is a crossover temperature, probably the transition temperature from liquid to crystal-like solid, for water confined in LGPs or SGPs. According to the work by Limmer and Chandler,[33] at the normal pressure, the melting temperature $T_m \approx 250$ K for water confined in a pore whose radius is 3 nm, corresponding to the average pore size of LGPs (3 nm∼12 nm) and SGPs (1 nm∼3 nm), while $T_m \approx 0$ the radii of pores < 1 nm, corresponding to the size of IGPs. Thus, the dynamic heterogeneities below and above the temperature 250 K are only for water confined in LGPs and SGPs, not for water ultra-confined in IGPs. Experimental evidence of the crossover temperature near 250 K has also been described for water confined in MCM44,[34] which is a two-dimensional hexagonal arrangement of cylindrical pores of uniform size with a diameter of 4.4 nm.

To give more evidence of the crossover temperature at 250 K, figures 5(b) and 5(d) show the HWHM $\Gamma_1(Q)$ and $\Gamma_2(Q)$ calculated from Eq. (5) by using the fitted values of D_{t1}, D_{t2}, τ_{01}, and τ_{02}. It can be seen that the minimum values of $\Gamma_1(Q)$ appear at 250 K for the measured temperature from 230 K to 280 K. This indicates once more that different dynamical behaviors are present below and above 250 K for the water confined in LGPs and SGPs. It is possible that the temperature 250 K can be explained as the liquid-to-crystal-like transition temperature, appearing in water confined in the LGPs and SGPs contained in C–S–H gel samples with a 30% water level.

Comparing the values of $\Gamma_1(Q)$ and $\Gamma_2(Q)$ in Figs. 5(b) and 5(d), it can also be seen that the values of $\Gamma_1(Q)$ are ten times those of $\Gamma_2(Q)$, indicating that the water confined in LGPs and/or SGPs is the main component to induce the QENS spectral broadening.

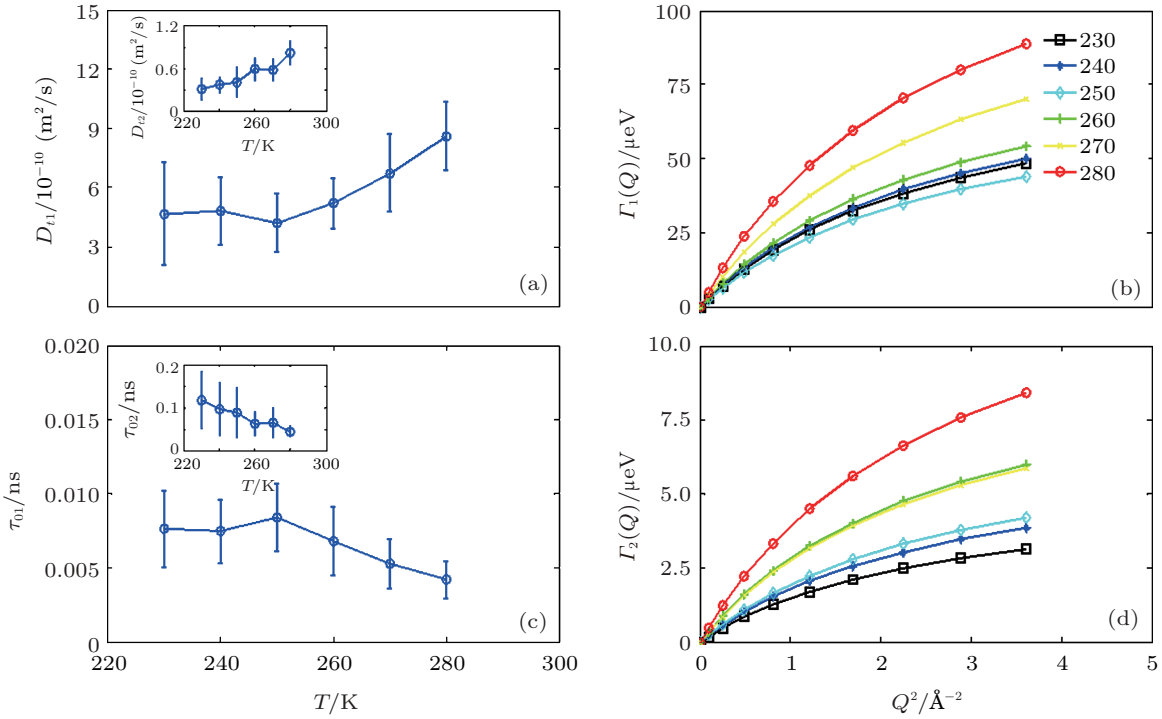


Fig. 5. (color online) Parameters of water confined in LGPs and SGPs and ultra-confined in IGPs for C–H–S gel samples with 30% water content. (a) The self-diffusion coefficient D_{t1} and D_{t2}, (b) the HWHM $\Gamma_1(Q)$, (c) the average residence time τ_{01} and τ_{02}, (d) the HWHM $\Gamma_2(Q)$.

5. Conclusions

In this work, by using the EDM to fit the measured QENS spectral data, we can obtain remarkably well fitted QENS spectra from C–S–H gel samples not only at small Q ($Q \leq 1$ Å^{-1}) but also at large Q. Several parameters of A, BWI, D_{t1}, D_{t2}, τ_{01}, τ_{02}, MSD, $\Gamma_1(Q)$ and $\Gamma_2(Q)$, characterizing the dynamic behaviors of water contained in the C–S–H gel, are extracted. Most of these parameters are new and different from those fitted by using RCM in our previous work,[7] except the A corresponding to the p in Ref. [7]. The A and p have the same values including the errors. The fitted parameter BWI shows that the proportion of the bound/immobile water increases with reducing the measured temperature and the water content. The values of MSD decrease with increasing Q. By the MSD, we can make a distinction among confined water, ultra-confined water, and bound/immobile water in C–S–H gel samples. When Q is small, the larger MSD belongs to the confined water in the LGPs and/or SGPs. As Q increases, the MSD gradually decreases, which corresponds to the ultra-confined water in the IGPs. As Q increases continually, the MSD tends to be the smallest value, which is identical for all the C–S–H gel samples, denoting that the MSD is attributed to the bound/immobile water. All the MSD results are the same as those of our previous work[24] for the fitting of QENS spectra from Portland cement pastes by using JRM. Furthermore, we can show that the parameters of D_{t1}, τ_{01}, and $\Gamma_1(Q)$ change abruptly at temperature 250 K for C–S–H gel samples with a 30% water level, while the phenomenon does not emerge for all of the parameters of D_{t2}, τ_{02}, and $\Gamma_2(Q)$. This means that the water confined in LGPs or SGPs below and above 250 K show different dynamic behaviors. The temperature 250 K can be explained as crossover temperature passing from liquid to crystal-like transition for water confined in LGPs or SGPs, which is consistent with the results in Refs. [8], [9], [31]–[34].

The above results show that the EDM can be used to fit the QENS spectra from C–S–H gel samples for the whole Q range. The fitted parameters are mostly different from those by RCM used in previous work.[7] These parameters describe the dynamic behaviors of water in C–S–H gel samples. The fitted MSD of water changes with the measured Q, and thus the water can be classified as the confined water, the ultra-confined water and the bound/immobile water, respectively. The fitted D_{t1}, τ_{01}, and $\Gamma_1(Q)$ show that a liquid-to-crystal-like transition behavior occurs at 250 K for the water confined in LGPs and/or SGPs with pore size $>$ 1 nm.

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