An Improved Model for Fitting QENS Data from Cement

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Abstract

In the previous study, we used Jump-diffusion and Rotation-diffusion Model (JRM) to fit the Quasi-Elastic Neutron Scattering (QENS) data from a magnesium silicate hydrate (MSH) cement sample, and found that the fitting effect was not satisfactory. In the region of neuton energy transfer |E| > 50 μeV, there is a significant difference between the fitting curve and the detected QENS data. So an improved model, revised Jump-diffusion and Rotation-diffusion Model (rJRM), was developed to fit the QENS data. Compared with the JRM fit , the rJRM fit is better. The rJRM is suitable to fit the QNES data in whole range of detected neutron scattering vector Q and neutron energy transfer E. However, the rJRM was too complex, so its simple model (srJRM) was used to fit the same QENS data in this paper. The fitting results show that srJRM fit is better than JRM fit. Compared with the rJRM fit, there are fewer parameters extracted from the srJRM fit. In addition, the values of fitted translational parameters are closer to those obtained by other relevant studies.

Keywords

An improved model; Quasi-Elastic Neutron Scattering (QENS); Dynamics of water.

1. INTRODUCTION

There are many models for Quasi-Elastic Neutron Scattering (QENS) spectra analysis [1]. Among them the JRM (Jump-diffusion and Rotation-diffusion Model) [2] [3] is the most commonly used model in QNES data fitting, because the JRM can comprehensively describe the diffusion motion of confined water molecules. However, when the JRM was used to fit QENS spectra from cement samples with μeV energy resolution, we found that the JRM should be improve to obtain better fit [3].

In our previous study, by fitting several group QENS data using JRM, we improved the JRM to an revised Jumping-diffusion and Rotational-diffusion Model (rJRM) [4] [5]. Figure 1 shows the fitted QENS data from MSH cement by using JRM and rJRM, respectively. From the JRM fit on left side subplot of Figure. 1, it can be seen that the blue fitting curve is significantly different from the red measured data in the region where |E| > 50 μeV. So the JRM fit is not good enough. From the rJRM fit on right side subplot of Figure. 1, it can be seen that the rJRM fit is better than that of the JRM fit. However, the rJRM is complex and has much more fitted parameters. Here we improed the rJRM to simple rJRM (srJRM) and use the srJRM to fit QENS data from cement.

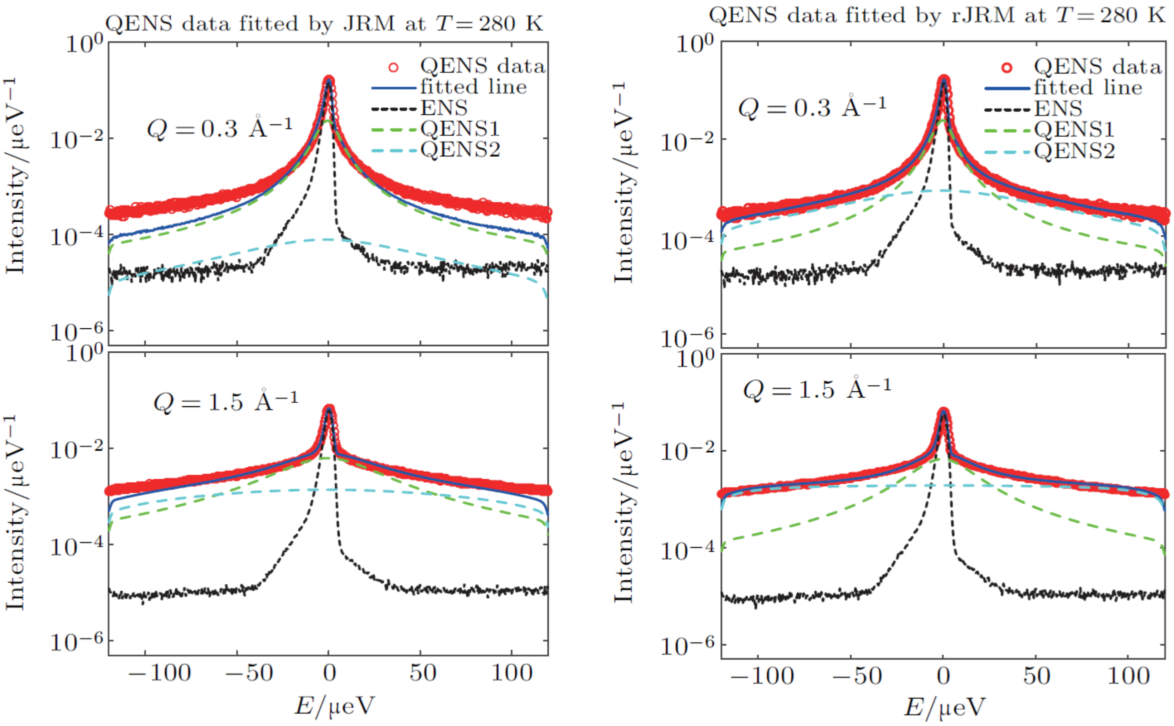

Figure 1. The fitted QENS data from MSH cement using JRM and rJRM[3][4], respectively

2. MATERIALS

The QENS data used in this paper were collected on magnesium silicate hydrate (MSH) cement sample, which were detected by professor chen's group on the high resolution backscatter instrument at the Spallation Neutron Source(SNS)[6] of Oak Ridge National Laboratory, USA. The energy resolution is 3.5 μeV. The neutron energy transfer range from -120 μeV to 120 μeV, and the neutron scattering vector Q ranges from 0.3 $Å^{-1}$ to 1.9 $Å^{-1}$. The measured temperature is from 210 K to 280 K. The information of QENS data is shown in table 1.

Table 1. The information of QENS data from MSH cement sample

Sample	measured temperature T (K)	neutron energy transfer E (μeV)	neutron scattering vector Q ($Å^{-1}$)
MSH cement	210 – 280	-120 – 120	0.3 – 1.9

3. FITTING MODEL

The used fitting model is srJRM, where the neutron scattering function is expressed as:

$$S(Q,E) = A\{C\delta(E) + (1-C)[S_T(Q,E) \otimes S_R(Q,E)]\} \otimes R(Q,E) + BG \tag{1}$$

where Q is the neutron scattering vector, E the neutron energy transfer, A the Debye–Waller factor, $\delta(E)$ the Dirac delta function, C the proportion of elastic scattering, $R(Q,E)$ the experimental resolution function, BG the flat background.

The translational diffusion scattering function $S_T(Q,E)$ can be expressed by the Lorentzian with half-width at half-maximum $\Gamma_T(Q)$[7]:

$$S_T(Q,E)=\frac{1}{\pi}\frac{\Gamma_T(Q)}{\Gamma_T^2(Q)+E^2} \tag{2}$$

$$\Gamma_T(Q)=\frac{\hbar D_t Q^2}{1+D_t Q^2\tau_0} \tag{3}$$

where $\hbar$ is the Plank constant, D_t the translational diffusion coefficient and τ_0 the average translational residence time.

The rotational diffusion scattering function $S_R(Q,E)$ can be expressed as[8][9]:

$$S_R(Q,E)=b_0^2 j_0^2(Qa_{OH})\delta(E)+\frac{1}{\pi}\sum_{l=1}^{3}(2l+1)b_l^2\, j_l^2(Qa_{OH})\frac{l(l+1)\hbar D_r}{[l(l+1)\hbar D_r]^2+E^2} \tag{4}$$

$$b_l^2=\begin{cases}4a_{coh}^2+2(1-\eta)a_{inc}^2, & l \text{ is even}\\ 2(1+\eta)a_{inc}^2, & l \text{ is odd}\end{cases} \tag{5}$$

where j_l (l = 0,1,2,3) is the spherical Bessel function, D_r the rotational diffusion coefficient, and a_{OH} the radius of gyration taken as the O–H distance (0.98 Å) in a water molecule. η is the statistical effect coefficient of the scattering cross section, and its value is between 0 and 1. Here η is taken as 0.5. a_{coh} and a_{inc} is the coherent and incoherent neutron scattering lengths, respectively. Their values adopted in the srJRM for H_2O are listed in Table 2.

Table 2. The square values of neutron scattering length

The square values of neutron scattering length	H_2O	H_2[8]	O_2[8]
$a_{coh}^2/barn$	0.307	0.142	0.33
$a_{inc}^2/barn$	6.35	6.34	0.02

4. RESULTS AND DISCUSSION

Figure 2 shows the fitted QENS data from cement by using srJRM, where ENS is the Elastic scattering part, QENS1 and QENS2 is the convolution of $S_T(Q,E)$ with the fisrt part and secend part of $S_R(Q,E)$, respectively. In figure 2, the red circle is the experimental data of QENS spectra, the blue solid line is the srJRM fitting curve, the black dotted line is the fitted ENS, the green dotted line is the fitted QENS1, the pink dotted line is the fitted QENS2, and the cyan dotted line is the fitted BG. The fitting curve is the sum of ENS, QENS1, QENS2 and BG. From figure 2, it can be see that the QENS data are fitted well for the two neutron scattering vector 0.3 $Å^{-1}$ and 1.5 $Å^{-1}$ at temperatures 230 K and 280 K. By comparing with Figure 1, it can be seen that the srJRM fit is better for Q = 0.3 $Å^{-1}$ and 1.5 $Å^{-1}$ at 280 K on the right two subplot in figure 2 than the JRM fit on the left two subplot in figure 1, and is comparable to the rJRM fit on the right two subplot in figure 1. By using srJRM, six parameters can be obtained: A, C, D_t, τ_0, D_r and BG, which are less than seven parameters abstracted from rJRM.

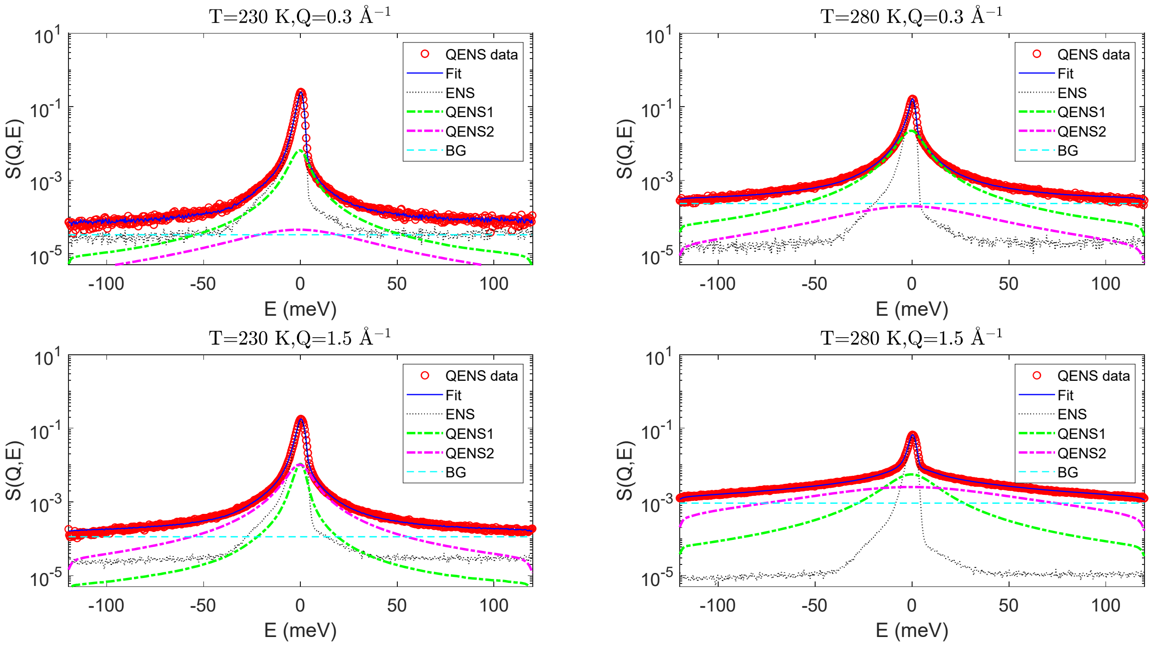

Figure 2. The fitted QENS data from MSH cement by using srJRM

Figure 3 shows the translational diffusion coefficient D_t obtained by rJRM and srJRM fitting. From Figure 3, it can be seen that the D_t decreases and then increases with the increase of temperature. In rJRM fit on left subplot of figure 3, the lowest value of D_t is at 230 K, while in srJRM fit on the right subplot of figure 3, the lowest value of D_t is between 220 K and 230 K.

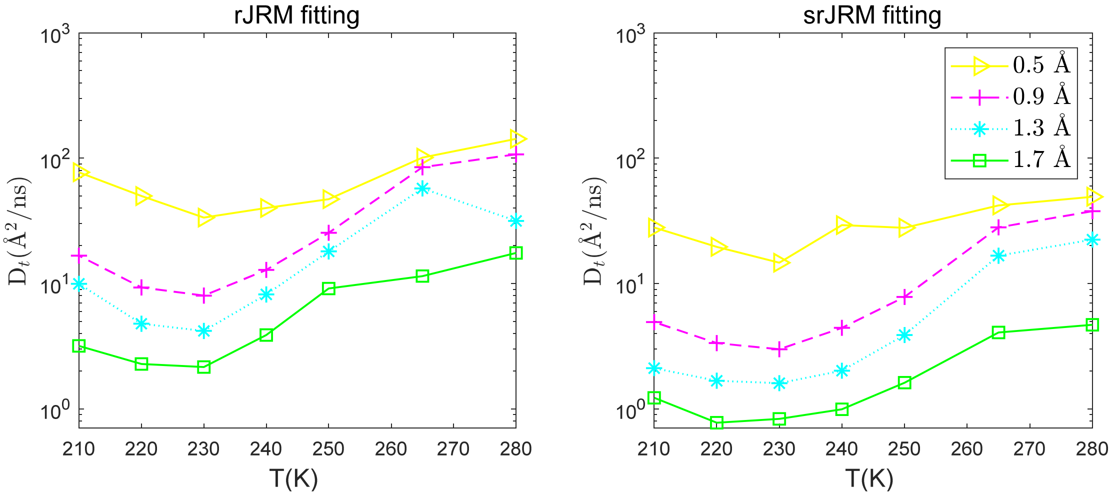

Figure 3. Parameter D_t obtained by rJRM fit (left) and srJRM fit (right)

Figure 4 shows the Rotational diffusion coefficient D_r obtained by rJRM and srJRM fitting. From the rJRM fit shown in left subplot of figure 4, it can be seen that the D_r first increases and then decreases with the increase of temperature. The maximum value of D_r is around 230 K. From the srJRM fit shown in right subplot of figure 4, the D_r first decreases and then increases with the increase of temperature. The lowest value of D_r is around 230 K. The variation of D_r abstracted from srJRM is consistent with the general thermodynamic phenomenon[10]. The value of D_r obtained by srJRM fit is in magnetude of $1-100\ ns^{-1}$, which are in the range of D_r mentioned by the related papers[2].

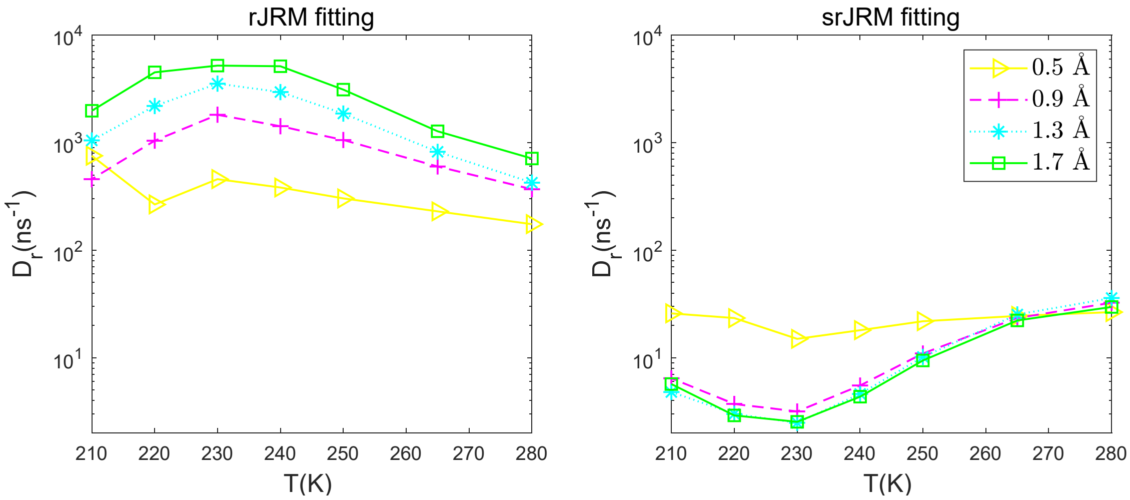

Figure 4. Parameter D_r obtained by rJRM fit (left) and srJRM fit (right)

5. CONCLUSIONS

In this paper, the QNES data cellected on MSH cement at the temperature ranged from 210 K to 280 K are fitted by the srJRM. The fitting results are better than those of JRM fitting, although they are comparable to rJRM fitting. The srJRM is simpler than rJRM, because of the number of fitting parameters reduced. Comparing with the rJRM fit , the values of D_t and D_r abstracted from the srJRM fit are more closer to those mentioned by the related research.

ACKNOWLEDGMENTS

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REFERENCES

[1] K. Zhao et al., “Quasi-elastic neutron scattering (QENS) and its application for investigating the hydration of cement-based materials: State-of-the-art,” Mater. Charact., vol. 172, no. June 2020, 2021.

[2] H. N. Bordello, L. P. Aldridge, and A. Desmedt, “Water dynamics in hardened ordinary portland cement paste or concrete: From quasielastic neutron scattering,” J. Phys. Chem. B, vol. 110, no. 36, pp. 17966–17976, 2006.

[3] H. Li, L. L. Zhang, Z. Yi, E. Fratini, P. Baglioni, and S. H. Chen, “Translational and rotational dynamics of water contained in aged Portland cement pastes studied by quasi-elastic neutron scattering,” J. Colloid Interface Sci., vol. 452, pp. 2–7, 2015.

[4] H. Li, Y. H. Chen, and B. Z. Tang, “A revised jump-diffusion and rotation-diffusion model,” Chinese Phys. B, vol. 28, no. 5, 2019.

[5] Y.-H. Chen, C.-X. Xiao, H. Li, E. Fratini, P. Baglioni, and S.-H. Chen, “Water dynamics in C–S–H and M-S-H cement pastes: A revised jump-diffusion and rotation-diffusion model,” Phys. B Condens. Matter, no. June, p. 413542, 2021.

[6] E. Mamontov and K. W. Herwig, “A time-of-flight backscattering spectrometer at the Spallation Neutron Source, BASIS,” Rev. Sci. Instrum., vol. 82, no. 8, 2011.

[7] K. S. Singwi and A. Sjölander, “Diffusive Motions in Water and Cold Neutron Scattering,” Phys. Rev., vol. 119, no. 3, pp. 863–871, Aug. 1960.

[8] V. F. Sears, “Theory of Cold Neutron Scattering By Homonuclear Diatomic Liquids: Ii. Hindered Rotation,” Can. J. Phys., vol. 44, no. 6, pp. 1299–1311, 1966.

[9] V. F. Sears, “Cold Neutron Scattering By Molecular Liquids: Iii. Methane,” Can. J. Phys., vol. 45, no. 2, pp. 237–254, 1967.

[10] C. E. Bertrand, Y. Zhang, and S. H. Chen, “Deeply-cooled water under strong confinement: Neutron scattering investigations and the liquid-liquid critical point hypothesis,” Phys. Chem. Chem. Phys., vol. 15, no. 3, pp. 721–745, 2013.

[11] P. Le et al., “Quasi-Elastic Neutron Scattering Study of Hydration Water in Synthetic Cement: An Improved Analysis Method Based on a New Global Model,” J. Phys. Chem. C, vol. 121, no. 23, pp. 12826–12833, 2017.