ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

A revised jump-diffusion and rotation-diffusion model

Hua Li(李华), Yu-Hang Chen(陈昱沆), Bin-Ze Tang(唐宾泽)

Citation: Chin. Phys. B . 2019, 28(5): 056105. **doi:** 10.1088/1674-1056/28/5/056105
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Recent progress on magnetic-field studies on quantum-spin-liquid candidates

Zhen Ma(马祯), Kejing Ran(冉柯静), Jinghui Wang(王靖珲), Song Bao(鲍嵩), Zhengwei Cai(蔡正蔚), Shichao Li(李世超), Jinsheng Wen(温锦生)
Chin. Phys. B . 2018, 27(10): 106101. **doi:** 10.1088/1674-1056/27/10/106101

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

Zhou Yi(易洲), Pei-Na Deng(邓沛娜), Li-Li Zhang(张丽丽), Hua Li(李华)
Chin. Phys. B . 2016, 25(10): 106401. **doi:** 10.1088/1674-1056/25/10/106401

A revised jump-diffusion and rotation-diffusion model

Hua Li(李华)†, Yu-Hang Chen(陈昱沆), and Bin-Ze Tang(唐宾泽)

Department of Physics, Jinan University, Guangzhou 510632, *China*

(Received 18 December 2018; revised manuscript received 20 March 2019; published online 19 April 2019)

Quasi-elastic neutron scattering (QENS) has many applications that are directly related to the development of high-performance functional materials and biological macromolecules, especially those containing some water. The analysis method of QENS spectra data is important to obtain parameters that can explain the structure of materials and the dynamics of water. In this paper, we present a revised jump-diffusion and rotation-diffusion model (rJRM) used for QENS spectra data analysis. By the rJRM, the QENS spectra from a pure magnesium-silicate-hydrate (MSH) sample are fitted well for the Q range from 0.3 Å^{-1} to 1.9 Å^{-1} and temperatures from 210 K up to 280 K. The fitted parameters can be divided into two kinds. The first kind describes the structure of the MSH sample, including the ratio of immobile water (or bound water) C and the confining radius of mobile water a_0. The second kind describes the dynamics of confined water in pores contained in the MSH sample, including the translational diffusion coefficient D_t, the average translational residence time τ_0, the rotational diffusion coefficient D_r, and the mean squared displacement (MSD) $\langle u^2 \rangle$. The rJRM is a new practical method suitable to fit QENS spectra from porous materials, where hydrogen atoms appear in both solid and liquid phases.

Keywords: revised jump-diffusion and rotation-diffusion model (rJRM), data analysis of quasi-elastic neutron scattering (QENS) spectra, dynamics of water, magnesium-silicate-hydrate (MSH) samples

PACS: 61.05.fg, 64.70.qj, 66.30.jj **DOI:** 10.1088/1674-1056/28/5/056105

1. Introduction

Quasi-elastic neutron scattering (QENS) has undergone remarkable development since the 1970s.[1] A QENS experiment measures the energy transfer (E) and momentum exchange (Q) between a neutron and a sample target. Because of the very large incoherent scattering cross section of a hydrogen atom as compared to any other element present in the investigated samples, QENS[2–4] is a powerful tool for studying the dynamics of water molecules in a confined environment. The fitted results of QENS spectra can provide information about both the long-time diffusive motions (on the time scale of 0.1 ns) and short-time rotational motions of water molecules contained in porous samples. So the analysis method of QENS spectra is important to obtain parameters explaining the dynamics of confined water.

As we know, there are mainly three types of theoretical models[5] used to fit QENS data: the empirical diffusion model (EDM),[6–8] the relaxed cage model (RCM),[4,9,10] and the jump-diffusion and rotation-diffusion model (JRM).[2,11,12] Although all the three models have been used to fit QENS spectra data, seldom of them can give well fitted QENS spectra both for $Q \leq 1$ Å^{-1} and $Q > 1$ Å^{-1} at the neutron energy transfer larger than 50 μeV.

The JRM combines both the translational and rotational motions of water, so it can give more comprehensive and related parameters describing the water contained in porous samples, but there still exist some approximations. In this paper, a revised JRM (rJRM) has been developed based on JRM by adding the contribution to the elastic part from the translational motion of water and taking into account the contribution of the neutron scattering lengths in Sears expansion to deal with the rotational motion. The new model of rJRM seems to give a better fitted line for a QENS spectrum from a pure magnesium-silicate-hydrate (MSH) sample at Q values 0.3–1.9 Å^{-1} and E from -120 μeV to 120 μeV. Two kinds of parameters can be extracted for QENS spectra fitted by the rJRM. One depicts dynamics of water confined in the MSH sample, and the other reflects the structure of the MSH sample.

2. Fitting methods of QEMS spectra

2.1. The jump-diffusion and rotation-diffusion model

The jump-diffusion and rotation-diffusion model has already been used to fit QENS spectra by Bordallo *et al.*[2] in 2006 and us in recent years.[11,12] We adopt this model, different from Bordallo *et al.*, by choosing the scattering function in the form of $S(Q,E)$ instead of $S(Q,\omega)$. The JRM can be stated as

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

where Q is the neutron scattering vector (momentum exchange), E the energy transfer of neutron, A the Debye–Waller factor (DWF), $\delta(E)$ the Dirac delta function, C the factor presenting the part of elastic contribution to the total QENS spectra, $(1-C)$ the factor denoting the quasi-elastic component in the whole QENS spectra, $S_T(Q,E)$ and $S_R(Q,E)$ the scattering functions contributed by the translational motion and

†Corresponding author. E-mail: tlihua@jnu.edu.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

rotational motion, respectively, $\otimes$ the convolution action, and $R(Q,E)$ the experimental resolution function.

In Eq. (1), the DWF[13] can be given as

$$A = \exp\left(-\frac{1}{3}\langle u^2\rangle Q^2\right), \tag{2}$$

where $\langle u^2\rangle$ is the mean square displacement (MSD).

The translational component $S_{\rm T}(Q,E)$ is usually modeled by a Lorentzian with a half-width at half-maximum (HWHM) $\Gamma_{\rm T}(Q)$ as

$$S_{\rm T}(Q,E) = \frac{1}{\pi}\frac{\Gamma_{\rm T}(Q)}{\Gamma_{\rm T}^2(Q)+E^2}. \tag{3}$$

According to the model of Singwi and Sjölander,[14] the Q-dependence of $\Gamma_{\rm T}(Q)$ in the random jump diffusion process can be depicted as follows:

$$\Gamma_{\rm T}(Q) = \frac{\hbar D_{\rm t}Q^2}{1+D_{\rm t}Q^2\tau_0}, \tag{4}$$

where $\hbar$ is the Plank constant, $D_{\rm t}$ the self-diffusion coefficient (translational diffusion coefficient), and τ_0 the average translational residence time between two jumps.

The rotational component $S_{\rm R}(Q,E)$ can be expressed by the Sears expansion[2,11,15] as

$$S_{\rm R}(Q,E) = j_0^2(Qa)\delta(E) + \frac{1}{\pi}\sum_{l=1}^{3}(2l+1)j_l^2(Qa) \times \frac{l(l+1)\hbar D_{\rm r}}{[l(l+1)\hbar D_{\rm r}]^2+E^2}, \tag{5}$$

where j_l ($l=0,1,2,3$) is the spherical Bessel function, $D_{\rm r}$ the rotational diffusion coefficient, and a the radius of gyration taken as the O–H distance (0.98 Å) in a water molecule.[2]

In order to show the JRM fitting, the QENS spectra from one sample previously studied[10] by using the new global model are reanalyzed, which is the pure MSH sample measured at 210–280 K and Q values 0.3–1.9 Å^{-1}. The QENS data were collected by Professor Sow-Hsin Chen's group at the high-resolution backscattering silicon spectrometer at the Spallation Neutron Source in Oak Ridge National Laboratory, details of which are given in Ref. [10]. Figure 1 shows the MSH QENS spectra fitted by using JRM for 230 K and 280 K at Q values of 0.3 Å^{-1} and 1.5 Å^{-1}, respectively. In Fig. 1, the fitted line of the measured QENS data can be stated as the sum of three parts of ENS, QENS1, and QENS2, which are corresponding to the $ACR(Q,E)$, $A(1-C)j_0^2(Qa)S_{\rm T}(Q,E)\otimes R(Q,E)$, and the rest of the expanded Eq. (1), respectively. The ENS is the signal from the immobile species, such as water or OH chemically bound in a sample. The QENS1 and QENS2 are the signals from mobile water confined in nanoscale pores in the sample.

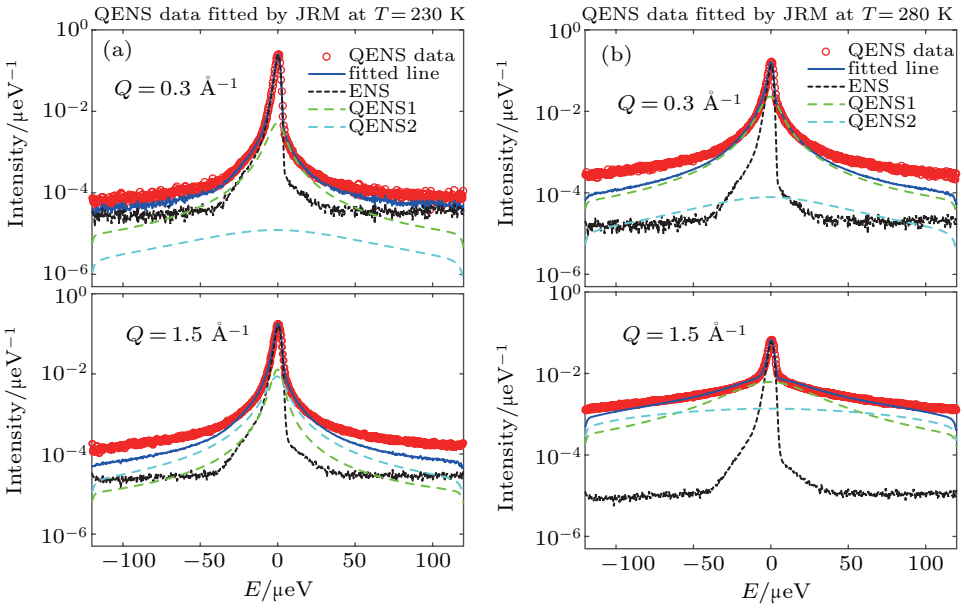


Fig. 1. MSH QENS spectra data fitted by JRM for temperatures (a) 230 K and (b) 280 K at Q values of 0.3 Å^{-1} and 1.5 Å^{-1}, respectively.

From Figs. 1(a) and 1(b), it can be seen that the QENS spectra are fitted well only for 230 K at 0.3 Å^{-1} (shown in Fig. 1(a)) and 280 K at 1.5 Å^{-1} (shown in Fig. 1(b)). Why? Is there a miss of some parts in the QENS spectra fitting? Re-examining the translational component in JRM, we find that the elastic fraction is accounted for only by a delta function representing the immobile water in Eq. (1). But there should be an elastic signal coming from the mobile water even without the presence of chemical bound water,[10,13,16] which is not included in Eq. (3). Re-examining the rotational component in JRM, the part of the QENS spectra due to localized rotational motion taken from the Sears expansion[15,17] should be a func-

tion of the neutron scattering lengths due to the interaction of the incident neutrons with the confined water molecules, which is also not included in Eq. (5). By adding the contribution to the elastic part from the mobile water and taking into account the contribution of the neutron scattering lengths in the Sears expansion, a revised JRM (rJRM) is developed in the next section.

2.2. The revised jump-diffusion and rotation-diffusion model

In the rJRM, the elastic part is added to $S_{\mathrm{T}}(Q,E)$ (instead of Eq. (3)) as

$$S_{\mathrm{T}}(Q,E) = p(Q)\delta(E) + (1-p(Q))\frac{1}{\pi}\frac{\Gamma_{\mathrm{T}}(Q)}{\Gamma_{\mathrm{T}}^2(Q)+E^2},$$
$$p(Q) = \left[\frac{3j_1(Qa_0)}{Qa_0}\right]^2, \tag{6}$$

where $p(Q)$ is the elastic component coming from the mobile water confined in pores,[8,10,13] j_1 the first order spherical Bessel function, and a_0 the confining radius.

In the rJRM, $S_{\mathrm{R}}(Q,E)$ includes the contribution of neutron scattering lengths[15,17] (instead of Eq. (5)) as

$$S_{\mathrm{R}}(Q,E) = x\left\{b_0^2 j_0^2(Qa)\delta(E) + \frac{1}{\pi}\sum_{l=1}^{3}(2l+1)b_l^2 j_l^2(Qa) \times \frac{l(l+1)\hbar D_{\mathrm{r}}}{[l(l+1)\hbar D_{\mathrm{r}}]^2+E^2}\right\}, \tag{7}$$

where

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

The a_{coh} and a_{inc} play the roles of effective coherent and incoherent neutron scattering lengths, $\eta = 0.95$ represents the effect of the nuclear statistics on the scattering cross section,[17] x is the parameter to cancel units of b_l^2. The taken values of a_{coh}^2 and a_{inc}^2 are obtained approximately from those of H_2 and O_2 and listed in Table 1.

Table 1. Effective neutron scattering lengths used in the rJRM fitting.

	Taken values	H_2[17]	O_2[17]
a_{coh}^2/barn	0.307	0.142	0.33
a_{inc}^2/barn	6.34	6.34	0.02

After the above two revisions based on the JRM, the expanded Eq. (1) can be shown as follows after inserting Eqs. (4), (6), and (7):

$$\begin{aligned} & S(Q,E) \\ &= ACR(Q,E) + A(1-C)p(Q)xb_0^2 j_0^2(Qa)R(Q,E) \\ &\quad + A(1-C)(1-p(Q))xb_0^2 j_0^2(Qa)\frac{1}{\pi}\frac{\Gamma_{\mathrm{T}}(Q)}{\Gamma_{\mathrm{T}}^2(Q)+E^2} \otimes R(Q,E) \\ &\quad + A(1-C)(1-p(Q))x\frac{1}{\pi}\frac{\Gamma_{\mathrm{T}}(Q)}{\Gamma_{\mathrm{T}}^2(Q)+E^2} \\ &\quad \otimes \frac{1}{\pi}\sum_{l=1}^{3}(2l+1)b_l^2 j_l^2(Qa)\frac{l(l+1)\hbar D_{\mathrm{r}}}{[l(l+1)\hbar D_{\mathrm{r}}]^2+E^2} \otimes R(Q,E) \\ &\quad + A(1-C)p(Q)x\frac{1}{\pi}\sum_{l=1}^{3}(2l+1)b_l^2 j_l^2(Qa) \\ &\quad \times \frac{l(l+1)\hbar D_{\mathrm{r}}}{[l(l+1)\hbar D_{\mathrm{r}}]^2+E^2} \otimes R(Q,E). \end{aligned} \tag{8}$$

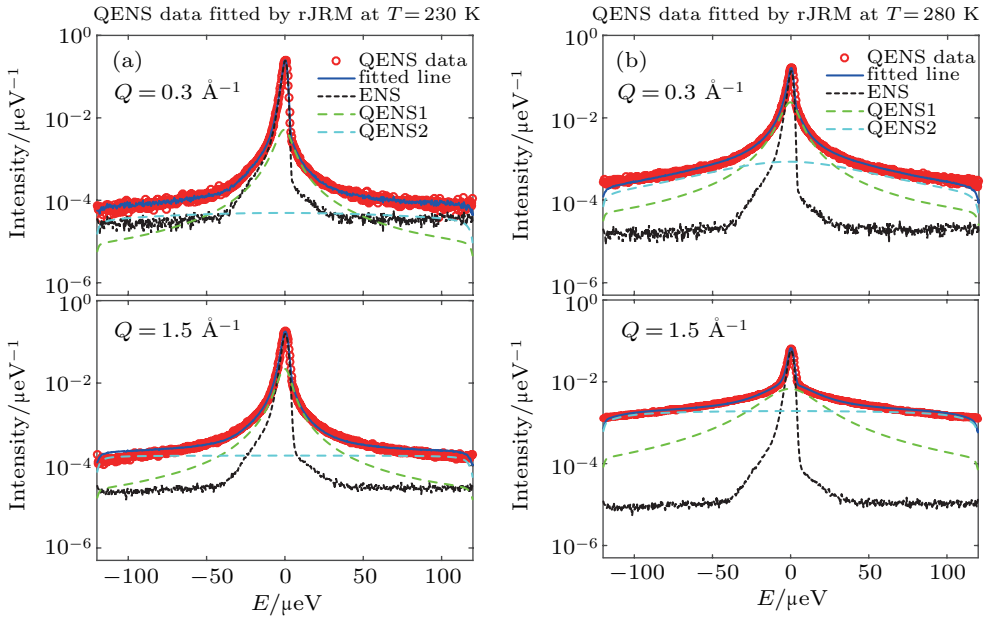


Fig. 2. MSH QENS spectra data fitted by rJRM for temperatures (a) 230 K and (b) 280 K at Q values of 0.3 Å^{-1} and 1.5 Å^{-1}, respectively.

A QENS spectrum can be fitted by the rJRM by summing three parts representing the ENS, QENS1, and QENS2, which are given respectively by the sum of the first and second items, the third item, and the rest items in Eq. (8). To test the rJRM fitting, the QENS spectra analyzed are the same as those fitted by JRM in Subsection 2.1 for the whole Q values, which are from the pure MSH sample measured at 210–280 K for Q of 0.3–1.9 Å^{-1}. Figure 2 shows the rJRM fitting for the MSH QENS spectra. From Figs. 2(a) and 2(b), it can be seen that the QENS spectra data are fitted well for E ranges from -120 μeV to 120 μeV both for high and low Q. Comparing with Figs. 1(a) and 1(b), it is found that the rJRM fitting is better for 230 K at 1.5 Å^{-1} (shown in Fig. 2(a)) and 280 K at 0.3 Å^{-1} (shown in Fig. 2(b)), because of the obvious higher contribution of the QENS2 due to accounting for the contribution of neutron scattering lengths in Eq. (7).

3. The extracted parameters

3.1. The fitted parameters

There are seven parameters extracted by using rJRM to fit a QENS spectrum, which are A, C, D_t, D_r, τ_0, a_0, and x. These fitted parameters can be divided into two types. One is structure parameters including C and a_0, which describe the immobile water fraction and the radius of pores existing in the sample, respectively. The other is parameters including DWF or MSD, D_t, D_r, and τ_0, which all describe the dynamics of mobile water confined in pores. Figure 3 shows the seven fitted parameters, with their fitted standard errors, and the MSD calculated by Eq. (2) as a function of the Q value (0.3–1.9 Å^{-1}) at 230 K and 280 K.

From Fig. 3(a), it can be seen that the DWF is nearly equal to 1 for Q from 0.3 Å^{-1} to 1.9 Å^{-1} at 230 K, but it is smaller than 1 and increases slightly with increasing Q at 280 K. This makes all the calculated MSD (in Fig. 3(b)) < 1.6 Å^2 for all the Q at 230 K, whereas the MSD decreases from 11.5 Å^2 down to near zero with increasing Q at 280 K. This is the first new result compared with the QENS spectrum fitted by RCM[4,10] or EDM,[6–8] where the MSD cannot be directly obtained because of the DWF taken approximately as unity in the data fitting process. From Fig. 3(c), it can be seen that the ratio of immobile water (mainly bound water) C decreases with increasing Q at both 230 K and 280 K, but it is larger at the lower temperature. Figure 3(d) shows that the x values all are close to 1 for both 230 K and 280 K. From Fig. 3(d), it can also be seen that the x values are slightly larger at the lower temperature 230 K for $Q > 1$ Å^{-1}. This may be attributed to the more active rotational motion for water molecules confined in smaller pores (larger Q) and at the lower temperature 230 K.

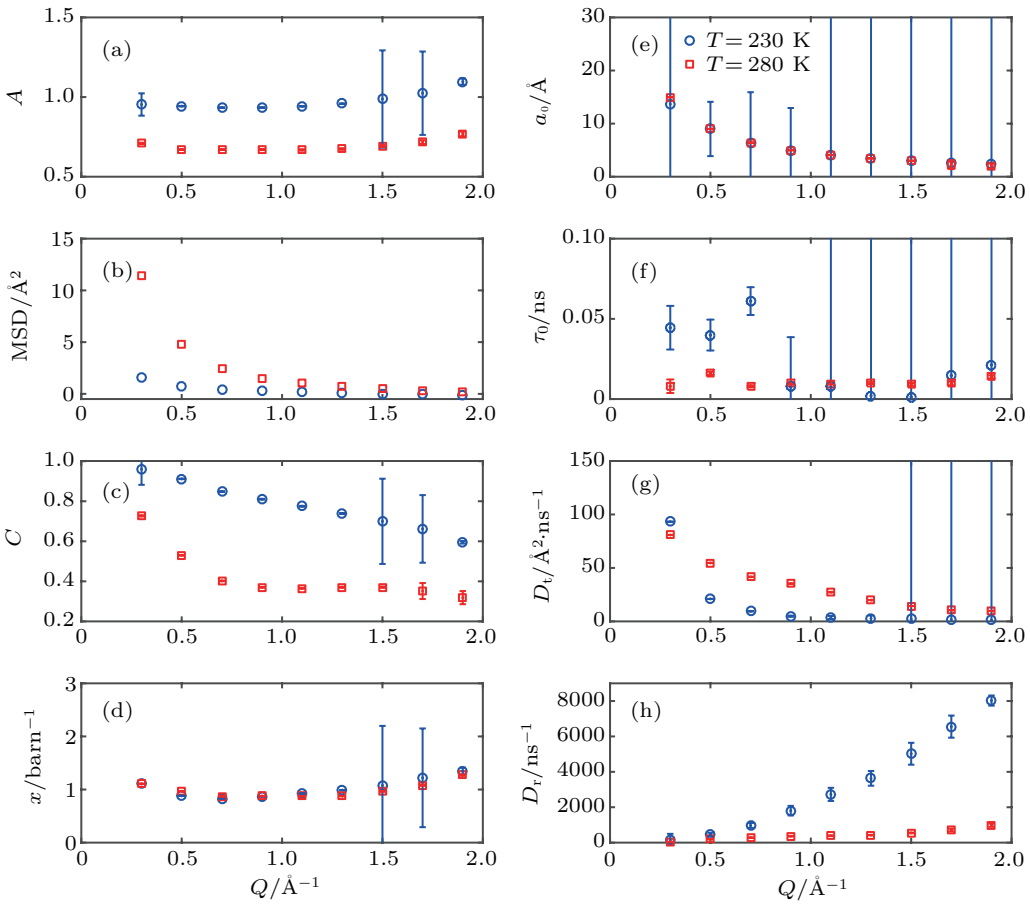


Fig. 3. (a)–(h) Seven fitted parameters with their fitted standard errors and the calculated MSD versus scattering vector at two temperatures of 230 K and 280 K.

Figure 3(e) shows that the fitted a_0 formed in the MSH sample decreases with increasing Q, and its value is almost the same at 230 K and 280 K for the same Q. This can be explained from the fact that the larger radius is probed at the smaller Q, and the radius of a pore formed in the sample is unrelated to the measured temperature. This is the second new result that the structure parameter a_0 different with various Q can be extracted by the rJRM fitting, although its fitted standard error is larger for larger Q at lower temperature. This result will be discussed more in Subsection 3.2. From Fig. 3(f), it can be seen that τ_0 is smaller than 0.1 ns at 230 K and 280 K, and its fitted standard error is larger for the larger Q at the lower temperature. Figures 3(g) and 3(h) show the fitted parameters of D_t and D_r, which range 1–100 Å^2/ns and 40–8000 ns^{-1}, respectively. From Figs. 3(g) and 3(h), we can also see that D_t and D_r vary with increasing Q and different temperatures. The former decreases with increasing Q at a measured temperature, but the latter increases. The former values are smaller at 230 K than those at 280 K, but vice versa for the latter. Their fitted standard errors all are small except for D_t at lower temperature 230 K for larger Q. The decrease of parameter D_t with Q indicates the inactive translational motion of water molecules confined in smaller pores detected at larger Q. So do the lower values of D_t for water at lower temperature. Similarly, the behavior of parameter D_r in Q and temperature can be explained as more active rotational motion of water molecules in smaller pores and at lower temperature. The information about D_r is the third new result obtained by the rJRM fitting. More discussion about the D_r will be given in Subsection 3.2.

3.2. Discussion

Among the parameters describing the structure of the sample, we focus on the discussion about a_0. Figure 4(a) shows a_0 as a function of Q and T. It can be seen that the fitted a_0 ranges from 19 Å to 2.0 Å, which are smaller than the values of the neutron detected space $2\pi/Q$. From Fig. 4(a), it can be seen that a_0 is almost of the same value for the same Q at different T except for $T < 230$ K. It can also be seen that the larger the Q value, the smaller the a_0 value. The result indicates that the radius of pores contained in the MSH sample ranges from 2.0 Å to 19 Å for the QENS experimental detection. This is consistent with the result that the MSH and CSH globules are packed together in the similar way,[18] and there are pores (radius < 3 nm) existing in the MSH sample. The fitted parameter a_0 shows more information compared with the same MSH QENS data analyzed in Ref. [10] by the new global model, where the fitted a_0 is only the average radius of pores in the MSH sample.

Among the parameters describing the dynamics of confined water, we focus on the discussion about D_r. Figure 4(b) gives the fitted D_r as a function of Q and T. From Fig. 4(b), it can be seen that D_r ranges from 40 ns^{-1} to 8000 ns^{-1} and increases with the increasing Q at a given T, and it reaches peak values at 230 K. This shows distinctly that the rotational dynamics of confined water exhibits different behaviors below and above 230 K. The 230 K is a crossover temperature for rotational dynamics of water confined in pores of 2.0–19 Å. The result is new compared with the same MSH QENS data analyzed over rotational dynamics of confined water in Ref. [10] by the new global model, where the crossover at 230 K was not observed because the lowest temperature was taken as 230 K.

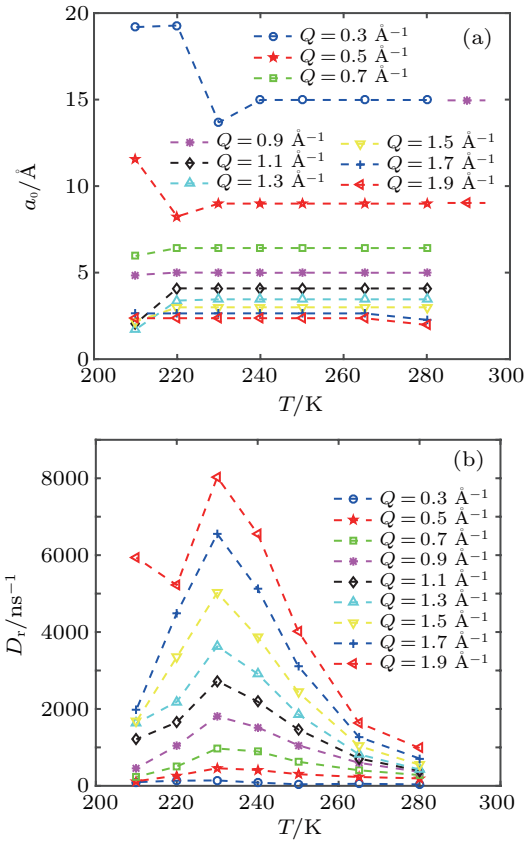


Fig. 4. The fitted parameters of (a) a_0 and (b) D_r versus scattering vector Q and measured temperature T.

4. Conclusion

We propose a rJRM model to fit QENS spectra data based on JRM model used before by adding the contribution to the elastic part from the translational motion of water and taking into account the contribution of neutron scattering lengths in Sears expansion to deal with the rotational motion of water. The rJRM seems to be better compared to JRM for fitting MSH QENS spectra measured at Q values 0.3–1.9 Å^{-1} and temperatures from 210 K to 280 K. Seven parameters (A, C, D_t, D_r, τ_0, a_0, and x) are extracted, which include not only those referring to the dynamics of confined water such as A, D_t, D_r, and τ_0, but also those revealing the structure of the sample such as C and a_0.

The rJRM model can give well fitted line for the MSH QENS spectra, not only for the whole Q range of 0.3–1.9 Å^{-1}, but also for the whole E range from -120 μeV to 120 μeV. Comparing with other models used to fit QENS spectra, especially the new global model,[10] the rJRM can obtain three new results for the extracted parameters. The first is the DWF or MSD that can be fitted directly. The second is nine values of a_0 indicating the radius 2.0–1.9 Å of pores existing in the MSH sample. The third is that the fitted D_r increases with the increasing Q at a measured temperature and reaches peak values at 230 K, showing that the 230 K is a crossover temperature for dynamics of confined water based on rotational motion. Although the rJRM is used to fit only one pure MSH sample here, in principle, it is expected useful also to analyze QENS spectra from porous materials, where hydrogen atoms appear in both solid and liquid phases. Further research on new sample is recommended.

Acknowledgments

We are particularly grateful to Professor Sow-Hsin Chen from Department of Nuclear Science and Engineering in Massachusetts Institute of Technology for providing help on the study of QENS spectra and Peisi Le for providing the MSH QENS spectra data fitted already by other method.

References

[1] Bee M 2003 *Chem. Phys.* **292** 121
[2] Bordallo H N, Aldridge L P and Desmedt A 2006 *J. Phys. Chem. B* **110** 17966
[3] Mamontov E, Wesolowski D J, Vlcek L, Cummings P T, Rosenqvist J, Wang W and Cole D R 2008 *J. Phys. Chem. C* **112** 12334
[4] Li H, Fratini E, Chiang W S, Baglioni P, Mamontov E and Chen S H 2012 *Phys. Rev. E* **86** 061505
[5] Eckold G, Schober H and Nagler S E 2010 *Studying Kinetics with Neutrons — Prospects for Time-Resolved Neutron Scattering* (London: Springer) pp. 19–75
[6] Thomas J J, FitzGerald S A, Neumann D A and Livingston R A 2004 *J. Am. Ceram. Soc.* **84** 1881
[7] Yi Z, Deng P N, Zhang L L and Li H 2016 *Chin. Phys. B* **25** 106401
[8] Viani A, Zbiri M, Bordallo H N, Gualtieri A F and Macova P 2017 *J. Phys. Chem. C* **121** 11355
[9] Chen S H, Liao C, Sciortino F, Gallo P and Tartaglia P 1999 *Phys. Rev. E* **59** 6708
[10] Le P S, Fratini E, Zhang L L, Ito K, Mamontov E, Baglioni P and Chen S H 2017 *J. Phys. Chem. C* **121** 12826
[11] Li H, Zhang L L, Yi Z, Fratini E, Baglioni P and Chen S H 2015 *J. Coll. Interf. Sci.* **452** 2
[12] Deng P N, Yi Z, Zhang L L and Li H 2016 *Acta Phys. Sin.* **65** 106101 (in Chinese)
[13] Bellissent-Funel M C, Chen S H and Zanotti J M 1995 *Phys. Rev. E* **51** 4558
[14] Singwi K S and Sjölander A 1960 *Phys. Rev.* **119** 863
[15] Sears V F 1966 *Can. J. Phys.* **44** 1299
[16] Wang Z, Le P S, Ito K, LeaTo J B, Tyagi M and Chen S H 2015 *J. Chem. Phys.* **143** 114508
[17] Sears V F 1966 *Can. J. Phys.* **44** 1279
[18] Chiang W S, Ferraro G, Fratini E, Ridi F, Yeh Y Q, Jeng U S, Chen S H and Baglioni P 2014 *J. Mater. Chem. A* **2** 12991