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Quasielastic neutron scattering of two-dimensional water in a vermiculite clay

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A well-characterized Na-vermiculite clay, containing zero, one, or two molecular layers of water between the clay platelets, has been studied by quasielastic neutron scattering (QENS). Experiments were carried out at a temperature of 300 K in two different scattering geometries; the clay platelets being at 45 and 135° angles to the incident beam in order to make the elastic Q -vector perpendicular and parallel, respectively, to the clay platelets for a scattering angle of 90° ($Q \approx 1.33 \text{ \AA}^{-1}$). The resulting QENS spectra show that almost no hydrogen motion occurs perpendicular to the clay platelets on the experimental time scale (about 2–40 ps). The two-H₂O layer vermiculite exhibits a planar rotational motion of water molecules, forming hydration shells around the Na ions, and a basically two-dimensional translational jump-diffusion motion. The translational motion was modeled using the Gaussian jump-length distribution model, resulting in a mean jump length of 1.1 Å and an average residence time of 2.3 ps. Using these values we obtain an effective diffusion coefficient of $8.8 \times 10^{-10} \text{ m}^2/\text{s}$, which is only a factor 2–3 lower than for bulk water. The correlation time of the rotational motion was estimated to approximately 27 ps. In the case of the one-H₂O layer vermiculite we were only able to observe a planar rotational motion with a rotational correlation time of 16 ps, i.e., faster than in the two-H₂O layer vermiculite. This suggests that a smaller number of water molecules are involved in the rotational process in the one-H₂O layer vermiculite, and furthermore that the translational motion, if existent, is too slow to be observed on the experimental time scale. © 2000 American Institute of Physics. [S0021-9606(00)70231-5]

I. INTRODUCTION

The behavior of water in confined geometries and near solid surfaces is of central importance in nature since most of the water in living organisms is closely associated (within approximately 5 Å) with different kinds of biomolecules.¹ The presence of this “biological” water is necessary for all living organisms and for a fundamental understanding of life. It is therefore essential to also elucidate the structure and dynamics of the associated water, both at ambient temperatures and in the supercooled regime. A comprehensive description of the microscopic properties and functional role of water associated with biomolecules is, however, a difficult task. Therefore, it is in many cases appropriate (and in some cases necessary) to use model systems which are geometrically more well-defined. In this work we use a Na-vermiculite clay² as such a model system.

The vermiculite clays have several advantageous properties for such studies: they have a layered structure, the water content can be controlled in a well-defined way (from one monolayer of water molecules to several hundred Ångströms) by the relative humidity and/or with ionic exchange.³ They also show several analogies with biological systems such as similar electrostatic properties of the surfaces and the well-known phase transition of hydrated proteins below

room temperature where water is phase separated from the protein.⁴ Thus, investigations of such systems may provide new information on the structure and dynamics of water of importance for biological systems.

The water dynamics in montmorillonite and vermiculite clays has been studied by quasielastic neutron scattering (QENS) since 1970.⁵ The first results^{5–7} indicated that the water diffusion coefficient was exponentially related to the inverse of the water-layer thickness, and that the diffusion coefficient for a water layer of about 6 Å, corresponding to two layers of water molecules, was about one order of magnitude lower than for bulk water, where the diffusion coefficient, D , at 295 K is about $D = 2.4 \times 10^{-9} \text{ m}^2/\text{s}$.^{6,8,9} However, due to the low energy resolution of the experiments (about 250 μeV) and the data analysis employed, more recent experiments have shown that the diffusion coefficients of the confined interlayer water were underestimated.^{8,10} Furthermore, the more recent investigations on Ca²⁺ (Ref. 8) and Li⁺ (Ref. 10) montmorillonites have shown that high-resolution QENS data cannot be fitted using only a Q -dependent quasielastic component, corresponding to translational jump diffusion, but also needs a Q -independent component arising from rotational motion of water molecules bound to the counterions.⁸ The present study on one- and two-H₂O layer Na-vermiculites shows good general agree-

ment with Refs. 8 and 10, but also some clear differences in the case of the one-H₂O layer sample. Moreover, since the stacks of clay platelets are larger and more directionally ordered (relative to each other) for the vermiculites, we have been able to perform a more detailed study where we also have included the directional dependencies of the translational and rotational jump-diffusions.

II. EXPERIMENT

The vermiculite crystals were from Eucatex, Brazil. Crystals about 30 mm² in area by 0.3 mm thick were washed and then treated for about a year with 1 M NaCl solution at 50 °C, with regular changes of solution, to produce a pure Na vermiculite, with the chemical formula¹¹



The vermiculite clays are unique in the sense that they are able to provide two-dimensional geometries with extremely thin and well-defined thickness of the water layer. The reason for this is that the interlayer Na⁺ ions have a strong tendency to hydrate, thereby forcing the clay platelets apart in a series of discrete steps. A totally dry Na-vermiculite crystal has a spacing between two consecutive clay layers (*d*-spacing) of approximately 10.6 Å. This *d*-spacing increases to 11.78 Å for a relative humidity up to about 70% and to 14.96 Å for a relative humidity above 70%.² If one subtracts the thickness of the rigid clay platelets there remains about 2 Å (i.e., the diameter of Na⁺) for the sodium ions in the dry 10.6 Å phase, about 3.2 Å (corresponding to one layer of water molecules) in the 11.78 Å phase, and approximately 6.4 Å (corresponding to two layers of water molecules) in the 14.96 Å phase. Thus, the thickness of the water layer can be regulated very accurately simply by varying the relative humidity.

In the case of the Na-vermiculite from Liano, Texas, which has a higher charge density than the Eucatex vermiculite studied here, there are an average of 2.1 water molecules per interlayer Na⁺ ion in the 11.78 Å phase, and all the hydrogen atoms are directed toward the adjacent clay platelets.² To obtain any hydrogen bonding between the water molecules one has to go to the 14.96 Å phase, where there are an average of 4.9 water molecules per interlayer Na⁺ ion, and only about half of these water molecules are orientated so that it can form a hydrogen bond to one of the clay surfaces, see Fig. 1(a).² Due to the lower charge density, and therefore also a lower concentration of intercalated Na⁺ ions, of the Eucatex vermiculite, there should be slightly more water molecules per interlayer Na⁺ ion in our case.

The quasielastic neutron scattering experiments on the Na-vermiculite clays were performed using the high-resolution inverted-geometry spectrometer IRIS at the pulsed neutron spallation source ISIS of the Rutherford Appleton Laboratory, UK.¹² Using the PG002 analyzers the incident wavelength was about 6.6 Å and the elastic energy resolution was 15 μeV [full width at half maximum (FWHM)], with a total energy window of ±0.5 meV. The 51 detectors were grouped into 17 groups of 3 detectors, giving a momentum transfer, *Q*, range of 0.46–1.84 Å⁻¹. Each sample was measured in two different scattering geometries [see Fig. 1(b)];

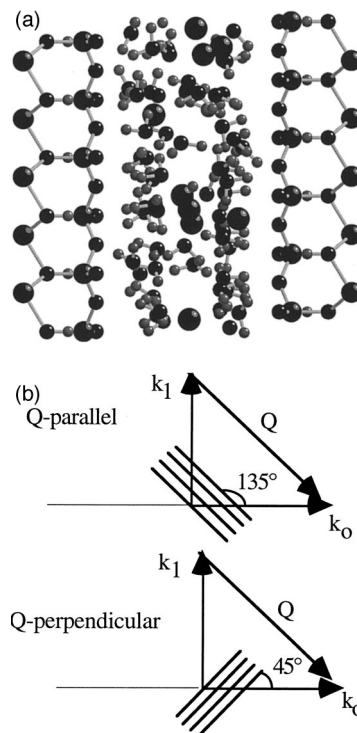


FIG. 1. (a) A plausible molecular snapshot of the clay platelets and the interlayer water and Na⁺ ions (large spheres) in the two-H₂O layer Na-vermiculite clay. The figure is taken from Ref. 23. The experimental geometries are schematically shown in (b).

the clay platelets being at 45 and 135° angle to the incident beam in order to make the elastic *Q*-vector perpendicular and parallel, respectively, to the clay platelets for a scattering angle of 90° (*Q* ≈ 1.33 Å⁻¹). The corrections for absorption, background, and can scattering were performed using the on-site standard program package IDA,¹³ which also was used for the subsequent analysis of the corrected data. The Na-vermiculite clay was measured in its three phases, with zero, one, and two layers of water molecules in the interplatelet region, respectively, at 300 K and in its latter fully hydrated state also at 265 K.

III. RESULTS AND ANALYSIS

A typical quasielastic neutron scattering spectra is presented in Fig. 2. The figure shows the spectrum for the two-H₂O layer Na-vermiculite clay measured at 300 K with the *Q*-vector parallel to the clay layers (*Q* = 1.36 Å⁻¹). The data are shown together with a least-square curve-fit of an elastic contribution and two Lorenzians convoluted with the resolution function. From the fitting procedure we obtain the intensities and full widths at half maximum (FWHM) of the two quasielastic components. Figures 3 and 4 show FWHM and intensity values, respectively, of the so-obtained quasielastic components as a function of *Q*². In Fig. 5 we show the ratios between quasielastic intensities and total scattering intensities of the one-H₂O and two-H₂O layer vermiculites.

A. The dry Na-vermiculite

In the case of the dry Na-vermiculite we did not expect to observe any significant quasielastic scattering from the

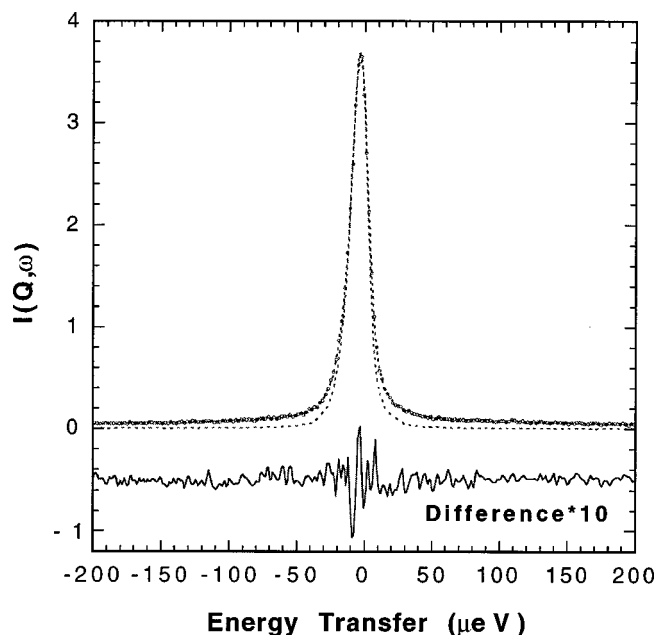


FIG. 2. Quasielastic neutron scattering spectra of the two-H₂O layer Na-vermiculite clay at $T=300$ K and $Q=1.36$ Å⁻¹. There is a clear broadening of the central peak compared to the resolution function (dotted line). The full line through the data is the best least-square fit as described in the text. The quality of the fit is shown below the spectrum as the difference (multiplied by a factor of 10) between the fitted line and the data.

rigid clay platelets or the intercalated Na⁺ ions. This was confirmed by the experiments where the clay platelets were aligned both parallel and perpendicular to the Q -vector at a scattering angle of 90°, showing that no atomic motion could be observed in any direction on the experimental time scale.

B. The one-H₂O layer Na-vermiculite

For the one-H₂O layer Na-vermiculite the data were satisfactorily fitted with a single Lorentzian convoluted with the resolution function. From Fig. 3(a) it is clear that the FWHM of this quasiline does not show any systematic Q^2 -dependence when the clay platelets are aligned parallel to the Q -vector at a scattering angle of 90°, indicating that only a rotational motion of hydrogen is present in the experimental time window. For the perpendicular geometry the FWHM shows the same lack of Q^2 -dependence except for the two data points at $Q^2 \approx 1.6$ Å⁻², where the broadening is considerably larger. This is probably an artifact due to the very low intensity in the perpendicular direction [see Fig. 5(a)], but may also be caused by a faster rotation in the perpendicular direction observed only in this geometry. More accurate measurements need to be performed before we are able to make a conclusive statement regarding this point. An average FWHM was estimated to be about 42 μeV [with the two low intensity data points neglected, see dashed line in Fig. 3(a)]. Using the formalism established by Dianoux *et al.*¹⁴ for rotational jump-diffusion we obtain a rotational correlation time of $\tau_1 = 16$ ps. Since the rotational correlation time for single water molecules has been estimated to be 1.5 ps,¹⁰ we attribute the observed rotational motion to a collective planar rotation of hydration water molecules around interca-

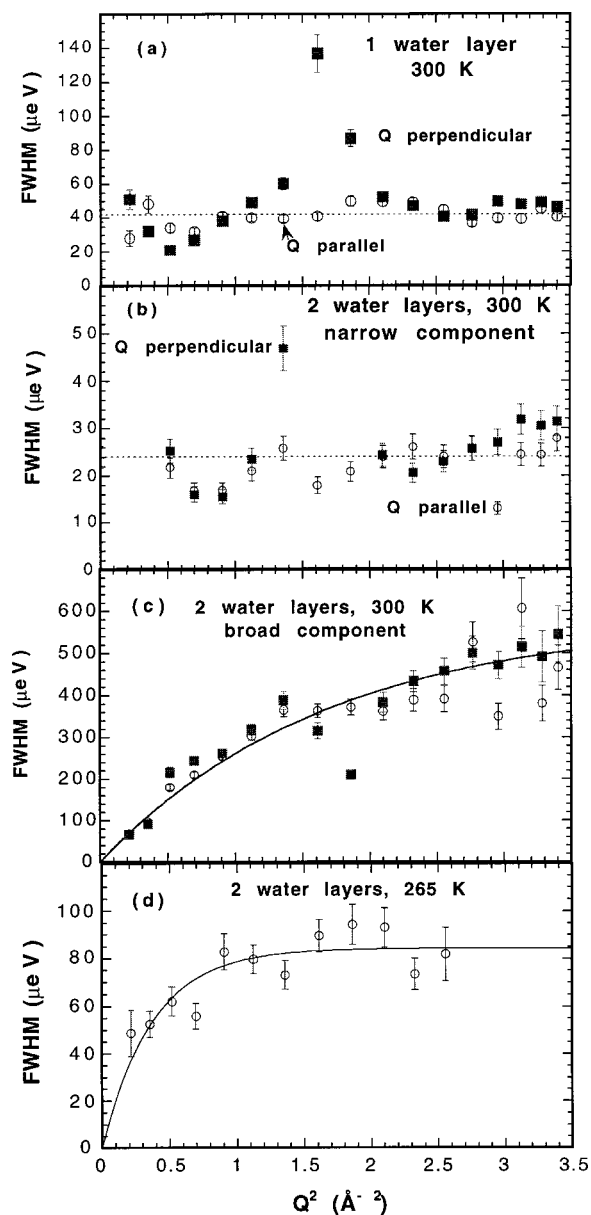


FIG. 3. FWHM values of quasielastic components as a function of Q^2 for water confined in Na-vermiculite clay. Filled squares and empty circles correspond to sample orientations where the clay platelets are aligned perpendicular and parallel, respectively, to the Q -vector at a scattering angle of 90°. (a) shows the Q^2 dependence of the single component in the one-H₂O layer vermiculite at 300 K. (b) and (c) show the narrow and broad components, respectively, in the two-H₂O layer vermiculite at 300 K, and (d) shows the only remaining component at 265 K.

lated Na ions in accordance with previous studies.¹⁵ Therefore, our value differs significantly (slower by a factor 10) compared to a rotational motion observed in Ref. 10 for a one-H₂O layer Li-montmorillonite. Better agreement is found in a comparison with Ref. 14, where they were able to resolve two rotational processes, with rotational correlation times of 6.9 and 26 ps, in a one-H₂O layer Li-vermiculite clay (see also Table I for a summary of the present and related previous results). The mean residence time, τ , can be related to the rotational motion according to the relation¹⁴

$$\tau = \tau_1 \left(1 - \cos \frac{2\pi}{N} \right), \quad (1)$$

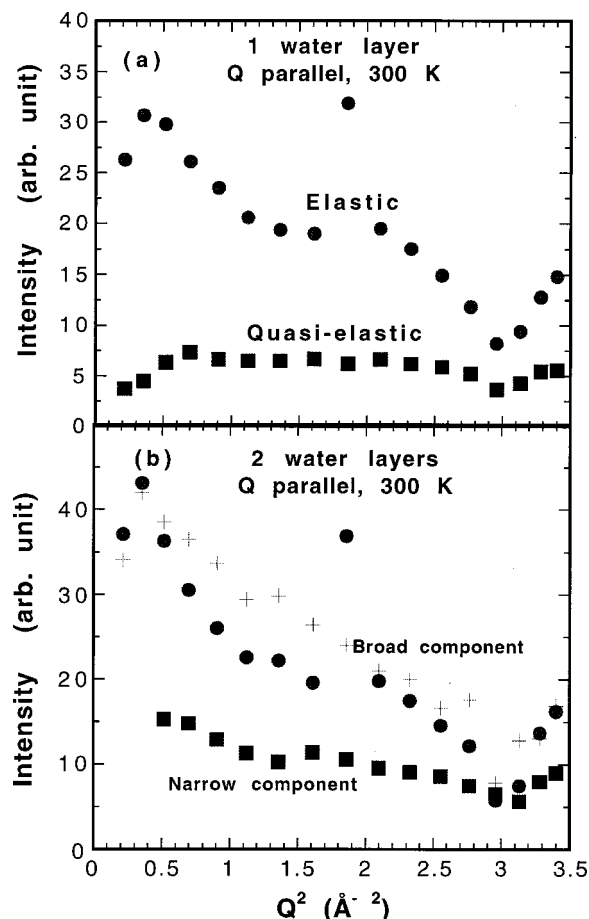


FIG. 4. Intensities of the elastic (filled circles) and quasielastic (filled squares and +) components as a function of Q^2 in the one- H_2O layer (a) and two- H_2O layer (b) Na-vermiculites at 300 K with the Q -vector parallel to the clay platelets at a scattering angle of 90° .

where τ also depends on the (unknown) number of sites, N , involved in the rotational process. However, since N is not exactly known it is not possible to give a value for the residence time, without further assumptions.

Figure 4(a) shows the intensities of the elastic and quasielastic components as a function of Q^2 for the clay platelets aligned parallel to the Q -vector at a scattering angle of 90° . It is evident from the figure that the intensity of the elastic component varies in a complicated way with a general decrease for increasing Q . Although the main decrease of intensity for increasing Q is caused by the increasing Debye-Waller factor, several other factors contribute to the complicated behavior. Particularly, one should note that accurate data corrections are difficult to perform when the scattering angle is approximately equal to the plane of the clay platelets (and the sample container), i.e., in this case for a scattering angle of about 135° ($Q^2 \approx 3.0 \text{\AA}^{-2}$). Generally, due to the sample geometries used, the data with Q perpendicular to the clay platelets (for a scattering angle of 90°) is less reliable for $Q^2 < 0.8 \text{\AA}^{-2}$, whereas the high Q data ($Q^2 > 2.5 \text{\AA}^{-2}$) are less reliable for the other geometry. The very high elastic intensity at $Q^2 \approx 1.85 \text{\AA}^{-2}$ is caused by a Bragg peak from the clay platelets. The intensity of the quasielastic component shows a weaker Q^2 -dependence, mainly due to the intensity decrease caused by the increasing

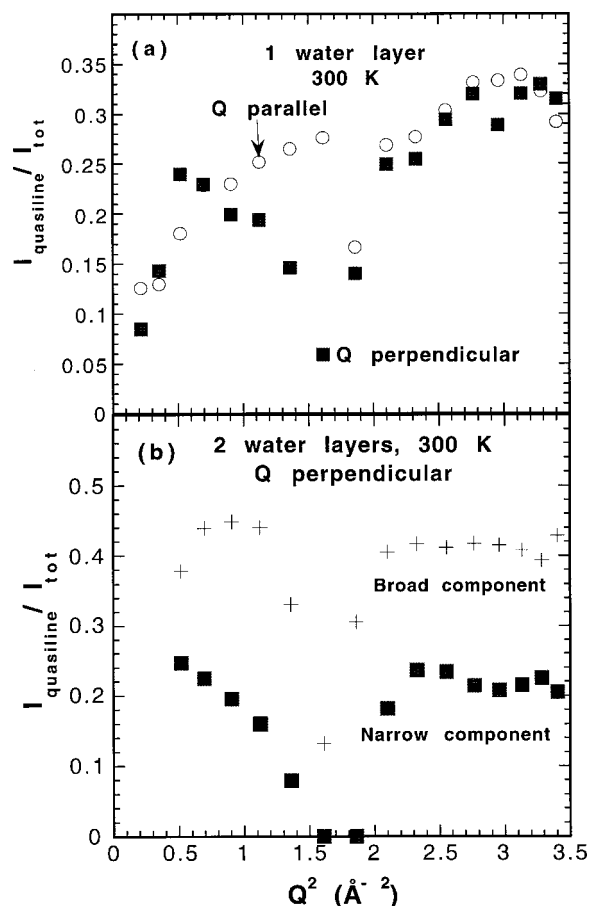


FIG. 5. Ratios between quasielastic intensities and total scattering intensity for (a) the one- H_2O layer vermiculite, where the clay platelets are aligned both perpendicular (filled squares) and parallel (empty circles) to the Q -vector at a scattering angle of 90° , and (b) the two- H_2O layer vermiculite, where the ratios are shown for the narrow (filled squares) and broad (+) quasielastic components with the clay platelets aligned perpendicular to the Q -vector at a scattering angle of 90° .

Debye-Waller factor being compensated by the Q -dependence of the intensity of the rotational motion, which gives rise to an increasing intensity with increasing Q . In Fig. 5(a) we show the ratio between the quasielastic intensity and the total scattering intensity. In the case when the clay platelets are aligned perpendicular to the Q -vector for a scattering angle of 90° , the intensity is substantially lower in the range $1.3 < Q^2 < 2.0 \text{\AA}^{-2}$ (i.e., when the scattering angle is $85 \pm 10^\circ$), indicating that the main rotational motion occurs in a plane parallel to the clay platelets. The general trend is otherwise that the ratio increases slightly with increasing Q for both sample geometries, mainly due to the decreasing elastic intensity with increasing Q .

C. The two- H_2O layer Na-vermiculite

Figures 3(b) and 3(c) show the broadenings of the two quasielastic components of the two- H_2O layer sample at 300 K. The FWHM values of the narrow component for Q perpendicular and parallel to the clay platelets at a scattering angle of 90° are shown in Fig. 3(b). Except for the data point at $Q^2 \approx 1.35 \text{\AA}^{-2}$ for the perpendicular sample geometry [where the intensity of the component is very low, see Fig.

TABLE I. Parameters characterizing the rotational and translational motion of water in clays at $T \approx 300$ K and bulk water at $T \approx 295$ K.

Sample	Rotational correlation time (ps)	Translational diffusion coefficient (m^2/s)	Residence time (ps)	Mean jump length $\langle r^2 \rangle^{0.5}$ (\AA)
1-H ₂ O Na-vermiculite	16			
2-H ₂ O Na-vermiculite	27	8.8×10^{-10}	2.3	1.1
same sample at $T = 265$ K		5.5×10^{-10}	16	2.3
1-H ₂ O Li-vermiculite ^a	6.9 (fast)			
	26 (slow)			
2-H ₂ O Li-vermiculite ^b	8.9	3.4×10^{-10}		
1-H ₂ O Li-montmorillonite ^c	1.5	4×10^{-10}	43	3.2
2-H ₂ O Li-montmorillonite ^c	1.5	7×10^{-10}	33	3.9
2-H ₂ O Ca-montmorillonite ^d		1.2×10^{-9}	10	2.7
Bulk water ^d		2.5×10^{-9}	1.4	1.4

^aReference 14.^bReference 15.^cReference 10.^dReference 8.

5(b)], there is no systematic Q -dependence, indicating that this slower process has a rotational origin. Its mean FWHM value is estimated to about $24 \mu\text{eV}$, see dashed line in Fig. 3(b), corresponding to a rotational correlation time¹⁴ $\tau_1 \approx 27$ ps. A similar slowing down, although slightly less, of the rotational motion in the two-H₂O layer vermiculite, compared to the one-H₂O layer, was also observed in Ref. 15 for a Li-vermiculite clay (see Table I). Finally, it should be noted that data for the two lowest Q -values do not show any clear sign of a resolved narrow component, perhaps making the values of the broader component less reliable for these Q -values.

The corresponding FWHM values of the broad quasi-elastic component are given in Fig. 3(c). The width of this quasielastic component shows a Q^2 -dependence that can be rather accurately modeled using the Gaussian jump-length distribution model.⁸ The Q -dependence of ΔE (=FWHM) of the broad Lorentzian corresponding to the translational motion can then be described by⁸

$$\Delta E = \frac{2\hbar}{\tau} [1 - \exp(-Q^2 \langle r^2 \rangle / 2)], \quad (2)$$

where $\langle r^2 \rangle$ is the mean square jump length and τ is an average residence time between two consecutive jumps. The analysis of the two-H₂O layer system gives a mean jump length of 1.1 \AA and a residence time of 2.3 ps at 300 K [see the least-square fit in Fig. 3(c)]. It should here be noted that these values remain the same even if the two data points at the lowest Q -values (which may show too small FWHM values due to the fact that the narrow component could not be resolved for these Q -values) are ignored in the fitting procedure. The values obtained should then be compared with the jump-diffusion process in bulk water, which shows a jump length of 1.4 \AA and a residence time of 1.4 ps at 295 K.⁸ If we convert the values to translational diffusion coefficients, using the relation $D = \langle r^2 \rangle / 6\tau$, we obtain $D = 8.8 \times 10^{-10} \text{ m}^2/\text{s}$ for the two-H₂O layer vermiculite and $D = 2.5 \times 10^{-9} \text{ m}^2/\text{s}$ (or $D = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$ from Ref. 9) for bulk water.⁸ Thus, from the present quasielastic neutron data it is evident that at least some of the confined water in the two-H₂O layer Na-vermiculite clay shows dynamics slower

by a factor of 2–3 compared to that of bulk water. It should also be noted that similar diffusion coefficients have been obtained for two-H₂O layer Li-montmorillonite ($D = 7 \times 10^{-10} \text{ m}^2/\text{s}$)¹⁰ and Ca^{2+} montmorillonite ($D = 1.2 \times 10^{-9} \text{ m}^2/\text{s}$)⁸ clays (see Table I for a summary).

In Fig. 4(b) we show the corresponding intensities of the elastic and two quasielastic components as a function of Q^2 in the case when the Q -vector is parallel to the clay platelets at a scattering angle of 90° . The broader component has an amplitude roughly twice the amplitude of the narrower component, indicating that the translational jump-diffusion process gives the dominant contribution to the total quasielastic intensity (particularly for low Q , i.e., for long distances). It is furthermore evident from Fig. 4 that the elastic intensity shows an almost identical Q^2 -behavior for the one- and two-H₂O layer vermiculites. Also, the intensity of the broad component has a similar Q^2 -dependence, indicating a weak Q -dependence of the intensity of this translational jump-diffusion process. The intensity of the narrow component decreases more slowly with increasing Q , although the intensity decrease is faster than in the case of the one-H₂O layer vermiculite, suggesting a more constant (i.e., less rapidly increasing) Q -behavior of the local rotational jump-diffusion process in the two-H₂O layer vermiculite. In Fig. 5(b) the ratios between the intensities of the narrow or broad quasi-elastic components, respectively, and the total scattering intensity for the clay platelets aligned perpendicularly to the Q -vector at a scattering angle of 90° , are shown. From the almost vanishing intensity at $Q^2 \approx 1.7 \text{ \AA}^{-2}$ (corresponding to a scattering angle of about 90°), particularly in the case of the rotational process (narrow component), it is clear that almost no atomic motion occurs in a direction perpendicular to the clay platelets.

Finally, in Fig. 3(d) we show preliminary FWHM values as a function of Q^2 for the only observable (within the experimental time window) quasielastic component in the two-H₂O layer Na-vermiculite clay at 265 K, when the Q -vector is parallel to the clay platelets at a scattering angle of 90° . At this temperature we do not detect any contribution from a rotational motion as it probably has become slower than the limit of the dynamical window. The Q^2 -dependence of the

FWHM of the observable component is in reasonable agreement with the Gaussian jump-length distribution model⁸ [see the least-square fit in Fig. 3(d)] for translational jump-diffusion. By comparison with the corresponding FWHM values at 300 K, given in Fig. 3(c), it is evident that the translational motion is slowed down at 265 K. From the least-square fit we obtain preliminary values of 2.3 Å for the jump length and 16 ps for the residence time, giving rise to a diffusion coefficient of $5.5 \times 10^{-10} \text{ m}^2/\text{s}$ at 265 K.

IV. DISCUSSION

The results of the present QENS study have shown that both the confinement of the water and the presence of interlayer Na ions affect the water dynamics. The reason for this is that both the oxygens at the clay surfaces and the interlayer Na ions tend to form relatively strong bonds to the hydrogens of the water molecules, giving rise to adsorbed hydration shells. This substitution of water–water hydrogen bonds reduces the average number of hydrogen bonds between the water molecules in the adsorbed layers¹⁶ and slows down the average diffusional motion of the confined water, particularly for the one-H₂O layer Na–vermiculite where the time scale of the translational motion appears to be slower than the experimental time scale. Also, in the case of the two-H₂O layer vermiculite the translational motion is slower than in bulk water; however, only by a factor of 2–3, which implies that at least some of the water shows dynamics relatively similar to bulk water. This is important since most of the interlayer water is prevented from crystallization¹⁷ and thus makes it possible to study the dynamics of supercooled water in the, for bulk water, inaccessible temperature range 150–235 K, where bulk water crystallizes.¹⁸ Hence, by investigating the dynamics of the confined water over a large temperature range it may be possible to gain insights in the dynamics of bulk water and to understand some of its peculiar properties, such as its density maximum at +4 °C.

We have recently performed such a wide temperature range (125–215 K) dynamical study of the supercooled interlayer water in the two-H₂O layer Na–vermiculite. This study¹⁹ showed that also its low-temperature dynamics seems to be similar (a factor of 2–3 in the speed of the dynamics is almost negligible considering that the time scale of the main relaxational dynamics of water changes by more than 13 orders of magnitude between room temperature and its glass-transition temperature at about 130 K^{20,21}) to that of bulk water i.e., both bulk water and our confined two molecular layers of water exhibit the same (within the deviations of slightly different experimental conditions) glass-transition temperature (130 K).^{19–21}

Turning to the directional and Q -dependences of the rotational and translational motions we note that the quasielastic components (particularly the narrow one in the two-H₂O layer vermiculite) are almost absent in the range $1.3 < Q^2 < 2 \text{ Å}^{-2}$ for Q perpendicular to the clay platelets (see Fig. 5), suggesting that basically no motion of hydrogens occurs in a direction perpendicular to the clay platelets. Thus, both the local rotational motion in the one- and two-H₂O layer vermiculites and the translational jump-diffusion process in the two-H₂O layer vermiculite occur almost entirely in a di-

rection parallel to the clay platelets. This is hardly surprising considering the high degree of confinement in the perpendicular direction.

It should also be noted that the rotational motion is faster in the one-H₂O layer vermiculite than in the two-H₂O layer vermiculite. This, in combination with the fact that the relative intensity of the rotational jump-diffusion process in the two-H₂O layer vermiculite increases more slowly with increasing Q than in the one-H₂O layer vermiculite (see Fig. 5), indicates that a larger number of water molecules are involved in the process in the case of the two-H₂O layer vermiculite. From these findings we attribute this rotational process to a collective planar rotational motion of water molecules around Na ions in the interlayer region, in agreement with previous interpretations of both QENS and NMR data.^{10,14,22}

Finally, we believe that the small interplatelet spacing, in combination with the presence of interlayer Na ions and the related hydrations shells, causes enough disorder and confinement of the interlayer water to prevent it from a global crystallization in the supercooled regime.¹⁷

V. CONCLUSION

From the present QENS study of water confined in a Na–vermiculite clay we are able to make the following conclusions:

- (1) The dynamics of the interlayer water is almost entirely in the two-dimensional (2D) plane parallel to the clay platelets (at least on the experimental time scale), although there are some weak indications of a fast rotational motion of single water molecules occurring in a direction perpendicular to the clay platelets.
- (2) The one-H₂O layer vermiculite exhibits a planar rotation of water molecules with a rotational correlation time of about 16 ps at $T = 300 \text{ K}$. The rotating water molecules are likely forming hydration shells around the Na ions.
- (3) The two-H₂O layer vermiculite exhibits both a collective planar rotational motion of water molecules, forming hydration shells around the Na ions, and a translational jump-diffusion motion, also mainly in the plane parallel to the clay platelets. The motional correlation time of the rotational process is about 27 ps and the residence time of the translational process is approximately 2.3 ps at $T = 300 \text{ K}$.
- (4) The translational diffusion in the two-H₂O layer vermiculite is rather similar to that in bulk water (slower only by a factor 2–3), suggesting that the short-range hydrogen bonding interactions are mainly determining the water dynamics.

ACKNOWLEDGMENTS

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- ¹H. D. Middendorf, *Physica B* **226**, 113 (1996).
- ²N. T. Skipper, A. K. Soper, and D. C. McConnell, *J. Chem. Phys.* **94**, 5751 (1991).
- ³M. V. Smalley, *Langmuir* **10**, 2884 (1994).
- ⁴J. D. Bryngelson, J. N. Onuchic, N. D. Socci, and P. G. Wolynes, *Proteins: Struct., Funct., Genet.* **21**, 167 (1995).
- ⁵S. Olejnik, G. C. Stirling, and J. W. White, *Spec. Discuss. Faraday Soc.* **1**, 188 (1970).
- ⁶R. J. Hunter, G. C. Stirling, and J. W. White, *Nature (London), Phys. Sci.* **230**, 192 (1971).
- ⁷S. Olejnik and J. W. White, *Nature (London), Phys. Sci.* **236**, 15 (1972).
- ⁸J. J. Tuck, P. L. Hall, M. H. B. Hayes, D. K. Ross, and C. Poinson, *J. Chem. Soc., Faraday Trans.* **80**, 309 (1984).
- ⁹J. Teixeira, M.-C. Bellissent-Funel, S. H. Chen, and A. J. Dianoux, *Phys. Rev. A* **31**, 1913 (1985).
- ¹⁰D. J. Cebula, R. K. Thomas, and J. W. White, *Clays Clay Miner.* **29**, 241 (1981).
- ¹¹H. Jinnai, M. V. Smalley, T. Hashimoto, and S. Koizumi, *Langmuir* **12**, 1199 (1996).
- ¹²C. J. Carlie and M. A. Adams, *Physica B* **182**, 431 (1992).
- ¹³W. S. Howells, Technical Report, Rutherford Appleton Laboratory, RAL-TR-96-006 (1996).
- ¹⁴A. J. Dianoux, F. Volino, and H. Hervet, *Mol. Phys.* **30**, 1181 (1975).
- ¹⁵C. Poinson, H. Estrade-Szwarczkopf, J. Conard, and A. J. Dianoux, *Physica B* **156–157**, 140 (1989).
- ¹⁶M. Rovere, M. A. Ricci, D. Vellati, and F. Bruni, *J. Chem. Phys.* **108**, 9859 (1998).
- ¹⁷R. Bergman, J. Swenson, L. Börjesson, and P. Jacobsson, *J. Chem. Phys.* (in press).
- ¹⁸H. E. Stanley, *MRS Bull.* **24**, 22 (1999).
- ¹⁹R. Bergman and J. Swenson, *Nature (London)* **403**, 283 (2000).
- ²⁰Y. P. Handa and D. D. King, *J. Phys. Chem.* **92**, 3323 (1988).
- ²¹G. P. Johari, A. Hallbrucker, and E. Mayer, *Nature (London)* **330**, 552 (1987).
- ²²J. Hougardy, W. E. E. Stone, and J. J. Fripiat, *J. Chem. Phys.* **64**, 3840 (1976).
- ²³N. T. Skipper *et al.*, in *ISIS Facility Annual Report* (1998), p. 47.