

Diffusion of benzene confined in the oriented nanochannels of chrysotile asbestos fibers

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We used quasielastic neutron scattering to study the dynamics of benzene that completely fills the nanochannels of chrysotile asbestos fibers with a characteristic diameter of about 5 nm. The macroscopical alignment of the nanochannels in fibers provided an interesting opportunity to study anisotropy of the dynamics of confined benzene by means of collecting the data with the scattering vector either parallel or perpendicular to the fibers axes. The translational diffusive motion of benzene molecules was found to be isotropic. While bulk benzene freezes at 278.5 K, we observed the translational dynamics of the supercooled confined benzene on the time scale of hundreds of picoseconds even below 200 K, until at about 160 K its dynamics becomes too slow for the μeV resolution of the neutron backscattering spectrometer. The residence time between jumps for the benzene molecules measured in the temperature range of 260 K to 320 K demonstrated low activation energy of 2.8 kJ/mol.

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I. INTRODUCTION

In recent years there has been considerable interest in studying the behavior of liquids in nanometer-sized pores. While water in confinement has attracted by far the most attention owing to its prominent role in biosystems, there is also a growing interest in the behavior of confined organic liquids, which is relevant in many applied areas such as catalysis and separation science. Techniques such as nuclear magnetic resonance and dielectric, optical, and neutron spectroscopy are employed to characterize the dynamics of the confined liquids (see Ref. 1 for a survey of recent experimental results). Among these techniques, quasielastic neutron scattering (QENS) benefits from the fact that the wavelength of cold neutrons is comparable with a typical diffusion jump distance. Thus the dependence of the quasielastic scattering on the scattering momentum transfer, Q , may yield information on the nature of the diffusion jumps.

Typically, QENS measurements of liquids confined within a macroscopic sample yield a powder-averaged scattering intensity. This is because even in the systems such as carbon nanotubes or MCM-41 silica, which possesses a hexagonal array of mesopores arranged as one-dimensional parallel channels, the length of the channels is limited by the particle size. In this work, we studied the dynamics of benzene confined in chrysotile asbestos (chemical formula $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) fibers (see Fig. 1). A typical diameter of pores in the fibers is a few nanometers, whereas an individual fiber length may be 1 cm or higher. Furthermore, the pores in the fiber are aligned macroscopically to form a set of one-dimensional parallel channels. This provides an interesting opportunity to study anisotropy of the dynamics of confined media along different directions by means of collecting the data with the scattering vector either parallel or perpendicular to the fibers axes. While our recent study of water

confined in chrysotile asbestos [2] has revealed no anisotropy in the water dynamics, which was attributed to the small size of a water molecule compared to the typical nanochannel diameter of 5 nm, one may hope to observe an anisotropy in the dynamics of larger organic molecules such as benzene confined in the same system of nanochannels.

In the limiting case of one-dimensional diffusion that takes place along the channels axes, one should expect no quasielastic broadening when the scattering vector is perpendicular to the channels axes. Instead, at sufficiently large Q values we have observed similar quasielastic broadening in both perpendicular and parallel directions, which indicates that the motion of benzene molecules can be viewed as a regular three-dimensional jump diffusion process. A larger than expected based on the benzene uptake fraction of the elastic scattering indicates a possible presence of benzene molecules whose dynamics is too slow to be observed in our experiment. For the mobile fraction of benzene molecules, the residence time of about 200–300 ps and the diffusion coefficient of the order of 10^{-10} m²/s have been measured in the temperature range of 260 K to 320 K. Both the diffusion coefficient and the residence time between the diffusion jumps demonstrate a very weak temperature dependence in

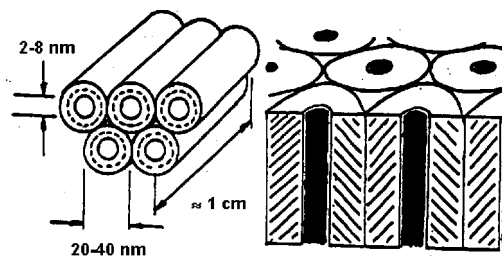


FIG. 1. A schematic picture of a bundle of chrysotile asbestos fibers.

this temperature range. In particular, we have obtained low activation energy of 2.8 kJ/mol for the temperature dependence of the residence time. The mobile fraction of benzene does not freeze even below 200 K. Instead, at about 160 K its dynamics slows down beyond the μeV (nanosecond) resolution of the neutron backscattering spectrometer.

II. EXPERIMENT

Chrysotile asbestos fibers with average outer and inner diameter of 28 nm and 5 nm, respectively, were obtained from the collection of Ioffe Physico-Technical Institute, St Petersburg, Russia. The macroscopic bundles of fibers had a cross section of up to $1 \times 2 \text{ mm}^2$ and a length of up to 1.5 cm. Prior to the filling with benzene, the fiber bundles were evacuated at 383 K, and their mass was determined to be 1.055 g. The fibers were then filled with benzene by means of submerging for several days and subsequent drying at 303 K in the air. The benzene uptake calculated as the mass difference between the sample filled with benzene and the sample after evacuation prior to filling was 0.028 g. This corresponds to about 1 C_6H_6 molecule per 10 molecules of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. For the benzene adsorbed only in the 5 nm intra-fiber channels, the maximum uptake of about 1 C_6H_6 molecule per 25 molecules of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ can be expected based on the chrysotile density of 2.56 g/cm^3 and benzene density of 0.879 g/cm^3 . The weight measurements are thus indicative of the benzene absorption in both the intra- and inter-fiber channels. For the ideal hexagonal close packing of fibers with the dimensions as studied in our experiment, the cross-section of the inter-fiber channels is 60% larger than that of the intra-fiber channels, and there are twice as many interfiber channels as there are intrafiber channels. However, the outermost surface of fibers is highly irregular, and the interfiber channels may be partially or fully filled with amorphous material, thus greatly reducing the channel cross section. Remarkably, the same ratio of 2.5 of the actual to expected liquid uptake was obtained in our previous study of water [2], where there was 1 H_2O molecule per 2 molecules of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, whereas 1 H_2O molecule per 5 molecules of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ would be expected to be present should water fill the 5 nm intrafiber channels only. Therefore, water in the previous and benzene in the current experiment fill the same pores in the chrysotile asbestos fibers.

Similarly to the previous experiment [2], the bundles of fibers were placed together onto a thin aluminum foil so that their axes were aligned and the bundles made up a single layer with a thickness of about 1 mm over the half of the foil. The foil was then folded forming a “flat plate” of bundles of fibers with the same direction of axes and securely placed into a thin aluminum sample holder. The sample holder was sealed with an indium O ring and mounted onto a top-loading closed-cycle refrigerator that used a helium exchange gas to minimize the temperature gradient through the sample. QENS experiments were carried out using the high-flux backscattering spectrometer (HFBS) at the National Institute of Standards and Technology (NIST) Center for Neutron Research [3]. In the standard

operation mode of the spectrometer, the incident neutron wavelength is varied via Doppler shifting about a nominal value of 6.271 \AA ($E_0=2.08 \text{ meV}$). After scattering from the sample, only neutrons having a fixed final energy of 2.08 meV are measured by the detectors as ensured by Bragg reflection from analyzer crystals. When operated with a dynamic range of $\pm 35 \mu\text{eV}$, the full width of the instrument resolution function at half maximum is about $1.2 \mu\text{eV}$. The spectra collected at $0.47 \text{ \AA}^{-1} < Q < 1.42 \text{ \AA}^{-1}$ (at the elastic channel) at 320 K, 300 K, 280 K, and 260 K were used in the data analysis. In addition, the spectrum collected at 100 K was used to determine the sample-dependent resolution function. In the alternative operation mode of the spectrometer called fixed-window mode, the Doppler drive was stopped, and only the elastic scattering intensity was collected while the sample temperature was ramped down from 310 K to 100 K at a rate of 0.5 K/min. The energy resolution of the HFBS in this mode of operation is about $0.8 \mu\text{eV}$. The fixed-window mode is especially useful for studying phase transitions such as freezing or melting.

In order to probe the anisotropy of the benzene dynamics, all the measurements reported in this paper were performed with two different orientations of the “flat plate” made of the bundles of fibers with respect to the scattering vector. In the first orientation, the fibers made 45° angle to the incident beam in order to make the elastic Q vector parallel to the axes of fibers for the scattering angle of 90° ($Q=1.42 \text{ \AA}^{-1}$). The elastic Q vectors for the other scattering angles thus had nonzero projections onto the directions of the fibers axes. Throughout the paper, we depict the data obtained in this geometry with open symbols, and, for the sake of simplicity, call this geometry “ Q -parallel.” The second orientation was obtained from the first one by means of rotating the sample by 90° about the axis perpendicular to the “flat plate” in the horizontal plane. In this orientation, the elastic Q vectors for all scattering angles are perpendicular to the fibers axes. The data obtained in this geometry are depicted with filled symbols, and the geometry is called “ Q -perpendicular.” The same terminology for the “ Q -parallel” and “ Q -perpendicular” orientations was used in our earlier study of water in chrysotile asbestos [2]. Compared to that study of confined water, the fraction of hydrogen atoms in the sample which are potentially mobile as opposed to immobile structural hydrogen atoms was lower (6/46 for benzene vs 2/10 for water). In fact, the fraction of the quasielastic scattering in the signal was even lower, as will be discussed below. In order to obtain reasonable statistics, we thus had to use detector grouping to combine the data from the neighboring detectors. Therefore, we analyzed the data obtained at the effective Q values of 0.51 \AA^{-1} , 0.68 \AA^{-1} , 0.93 \AA^{-1} , 1.16 \AA^{-1} , and 1.37 \AA^{-1} .

III. RESULTS AND DISCUSSION

The elastic scattering intensities measured as a function of temperature in the course of cooling down and summed up over all Q values are presented in Fig. 2. Except for an arbitrary vertical offset, no significant anisotropy between the data obtained in the “ Q -parallel” and “ Q -perpendicular”

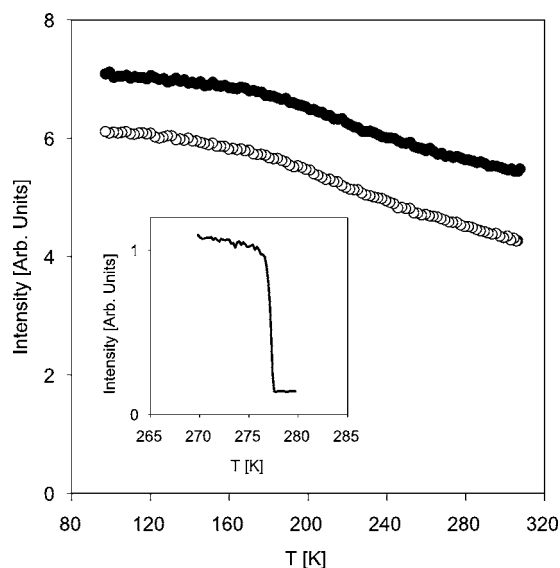


FIG. 2. The elastic scattering intensity measured in the fixed-window mode as a function of temperature and summed up over all Q values. Open circles: “ Q -parallel” orientation. Filled circles: “ Q -perpendicular” orientation. An arbitrary vertical offset of the baselines is applied for clarity. Inset: freezing of bulk benzene sample measured in the fixed-window mode shown for comparison.

orientations could be observed. It is evident that no freezing of confined benzene, similar to that observed for a bulk benzene sample and shown in the inset, could be observed. Instead of the abrupt increase due to freezing as demonstrated by bulk benzene, the elastic intensities measured in the fixed-window mode exhibit a gradual increase as the sample is cooled down, with a marked decrease in the slope at about 160 K. This behavior is indicative of the presence of quasi-elastic signal with the width that decreases as the temperature is decreased until it becomes too narrow for the resolution of the spectrometer at about 160 K. Below this temperature, the QENS signal can no longer be distinguished from the elastic signal, and the increase in the elastic scattering intensity as the temperature is further decreased is merely due to the Debye-Waller factor.

The scattering intensities measured at $Q=1.37 \text{ \AA}^{-1}$ at four temperatures are shown in Fig. 3 along with the data collected at 100 K, which represents the resolution function. In a typical QENS experiment, the quasielastic signal narrows as the temperature is decreased, indicating slower motion of the mobile species. This trend, albeit weak, can be seen in Fig. 3, where the QENS signal at 320 K seems to be broader than that at 260 K. As far as the anisotropy between the two orientations is concerned, it is not easy to see a trend because of the scattering in the data points. For the quantitative data analysis, we fit the data with the expression that includes a single Lorentzian with half width at half maximum, $\Gamma(Q)$, for the quasielastic broadening

$$I(Q, E) = C(Q) \left[x(Q) \delta(E) + [1 - x(Q)] \frac{1}{\pi} \frac{\Gamma(Q)}{E^2 + \Gamma^2(Q)} \right] + B_1 E + B_2 \quad (1)$$

that was convolved with the spectrometer resolution func-

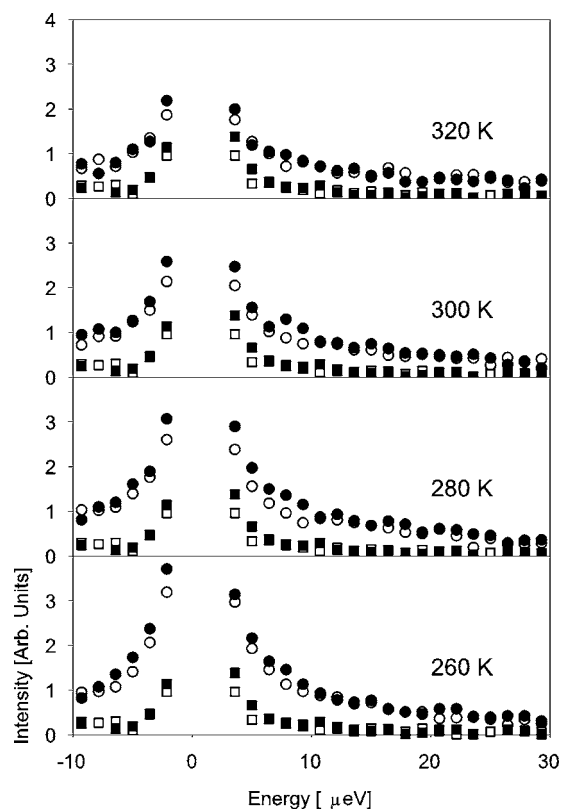


FIG. 3. The scattering intensities measured at $Q=1.37 \text{ \AA}^{-1}$. The energy range and the elastic peaks at zero energy transfer are truncated to better demonstrate the quasielastic signal. The 100 K data used as a resolution function are plotted on every graph and shown with squares. Open symbols: “ Q -parallel” orientation. Filled symbols: “ Q -perpendicular” orientation.

tion. Here C is a scaling constant, x is the fraction of the elastic scattering, and the linear term $B_1 E + B_2$ describes the background originating from the scattering signal which is too broad for the dynamic range of the backscattering spectrometer. The elastic scattering originates predominantly from the immobile structural hydroxyl groups in $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. As we have mentioned in the previous section, the fraction of the elastic scattering of $40/46 \approx 0.87$ would be expected assuming that all the benzene molecules filling the nanochannels are mobile. In fact, we have observed even greater fraction of elastic scattering of about 0.95 as one can see in Fig. 4. The additional elastic scattering likely originates from the hydrogen atoms in surface silanol ($\text{Si}-\text{O}-\text{H}$) groups and possibly from benzene molecules in direct contact with the surface. Previous QENS experiments performed with small loadings of benzene in zeolites indicate that translational motion of benzene molecules in direct contact with the surface may be too slow to be resolved with the HFBS resolution in the temperature range of the current experiment. While a sufficiently wide quasielastic broadening (in the range of μeV) due to translational mobility of benzene in Na mordenite was observed at 300 K in the early study by Jobic *et al.* [4], for the translational diffusion of benzene in NaX zeolite the residence time of 210 ps and 330 ps, depending on the loading, was found at 350 K [5], whereas in NaY zeolite the residence time was 300 ps at

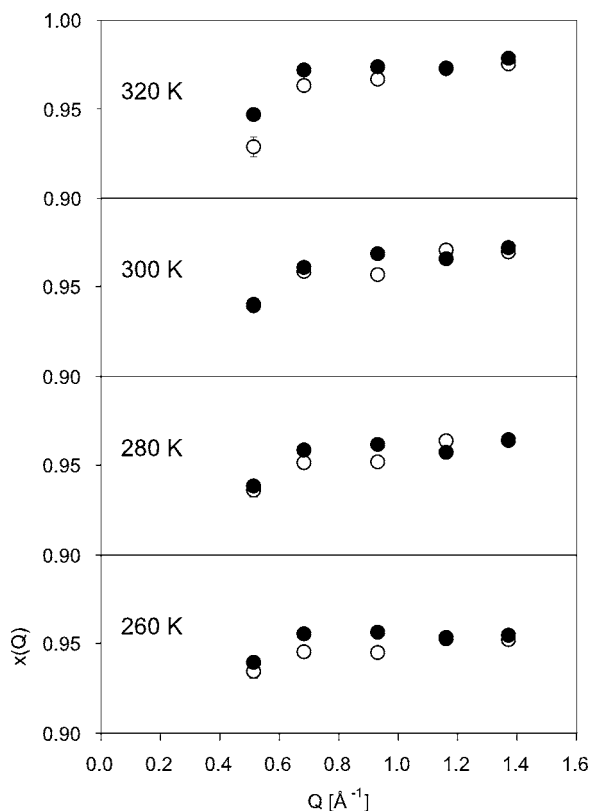


FIG. 4. The fraction of the elastic scattering, $x(Q)$, obtained using Eq. (1). Open symbols: “ Q -parallel” orientation. Filled symbols: “ Q -perpendicular” orientation.

450 K and 260 ps at 550 K [5]. While the activation energies of 16–17 kJ/mol [5] suggest that the translational motion of some surface benzene molecules, for example, benzene in NaX zeolite would still be observable with the resolution and temperature range of the current experiment, the increasing benzene loading seems to slow down the translational dynamics significantly due to benzene-benzene interaction [5]. In our experiment, where the surface is in contact with the bulk-like benzene phase rather than individual molecules, the translational motion of the molecules in contact with the surface may be further hindered compared to the experiments where isolated benzene molecules are in contact with the surface only. This may slow down their dynamics beyond the resolution of the instrument leading to the increasing fraction of the elastic scattering.

For the translational diffusion of confined mobile species, the elastic scattering from the mobile molecules approaches zero at high Q , and the fraction of the elastic scattering intensity in the total signal from the sample follows the Q dependence of the scattering intensity from the confining matrix. At low Q , there is an increase in the fraction of the elastic scattering due to the effect of confinement leading to increasing elastic scattering from the mobile molecules. An increase in the elastic scattering at low Q is also observed for localized motions such as a reorientational jump diffusion process. A small decrease in the fraction of the elastic scattering observed in our experiment at $Q=0.51 \text{ \AA}^{-1}$ (see Fig. 4) is just an artifact due to the special configuration of the low- Q detectors at the HFBS, which are characterized by a

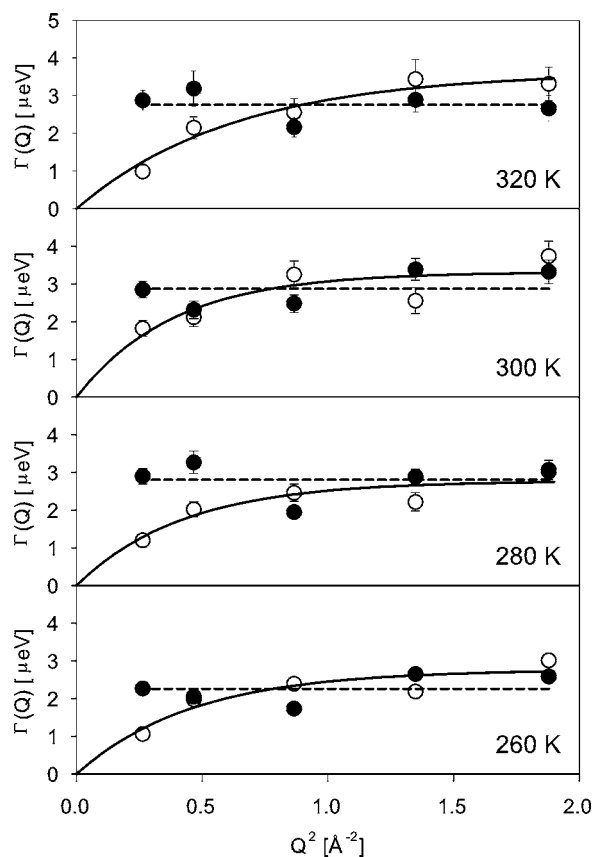


FIG. 5. The HWHM of the Lorentzian quasielastic broadening obtained using Eq. (1) fitted with Eq. (2) for the “ Q -parallel” orientation (open circles, solid lines) and with a Q -independent constant, \hbar/τ_{res} , for the “ Q -perpendicular” orientation (filled circles, dashed lines).

slightly worsened energy resolution and a higher background compared to the rest of the detectors [3].

The Q dependence of the half width at half maximum of the Lorentzian broadening is plotted in Fig. 5. For the “ Q -parallel” orientation, the QENS broadening grows with Q , indicating a translational diffusion process with a distribution of jump lengths. Assuming that the diffusion jumps take place in three dimensions, we fit the HWHM with the expression

$$\Delta E = \frac{\hbar}{\tau_{\text{res}}} [1 - \exp(-Q^2 \langle r^2 \rangle / 6)] \quad (2)$$

derived for a model with a Gaussian distribution of jump lengths, $P(r) = (2\pi)^{-1/2} (2r^2/r_0^3) \exp(-r^2/2r_0^2)$, where $\langle r^2 \rangle$ is the mean squared jump distance, and τ_{res} is the residence time between jumps [6]. An alternative model with an exponential distribution of jump lengths [7,8] is sometimes used, which yields the same high- Q limit (thus, the same residence time) for the QENS broadening. In fact, any translational jump diffusion process results in the QENS broadening of \hbar/τ_{res} at sufficiently high Q , which, in principle, allows unambiguous determination of τ_{res} .

For the “ Q -perpendicular” orientation, the QENS broadening at high Q is about the same as that for the “ Q -parallel”

TABLE I. Residence time, τ_{res} (in ps), between jumps for the translational jump diffusion of benzene molecules in chrysotile asbestos. Standard deviation values are shown in parentheses.

T (K)	Q perpendicular	Q parallel	Averaged between the two orientations
320	238 (33)	181 (17)	210 (25)
300	228 (38)	198 (25)	213 (32)
280	234 (42)	236 (25)	235 (34)
260	291 (49)	238 (26)	265 (38)

orientation, indicating the absence of anisotropy of the residence time between diffusion jumps in the directions parallel and perpendicular to the fibers axes. However, unlike that for the “ Q -parallel” orientation, the QENS broadening for the “ Q -perpendicular” orientation does not decrease at low Q , which seems to indicate that the motion of benzene in the directions perpendicular to the fibers axes is constrained. In the limit of low Q (that is, high intermolecular distances), a free diffusion DQ^2 law for the QENS broadening should be always observed, unless a localized character of the motion prevents diffusing molecules from accessing large distances even at long times. In the latter case, the QENS broadening remains a constant between zero Q and the value of Q corresponding to the dimension of the confinement volume [9,10]. For a diffusive motion within a circle of radius L , there should be two distinctive regimes with a crossover at about $Q_C = \pi/L$. At high Q values above Q_C , the QENS broadening should be similar to that observed for the unconfined diffusion (that is, it should approach the value of \hbar/τ_{res} at high Q), whereas below Q_C it should drop to about a value of $(\hbar/\tau_{res}) \times (\pi r_0^2/2L^2)$, where r_0^2 is the mean squared jump length. Also, a quick growth of the elastic incoherent structure factor (the fraction of the elastic scattering intensity) should be observed below Q_C . The fact that we observe neither a growth of the elastic scattering intensity as shown in Fig. 4 nor a drop in the QENS broadening for the “ Q -perpendicular” orientation as shown in Fig. 5 suggests that all our data points measured down to $Q=0.51 \text{ \AA}^{-1}$ are taken at $Q > Q_C$.

The effects of confinement should undoubtedly manifest themselves in the data measured in the “ Q -perpendicular” geometry at sufficiently low Q (below about 0.1 \AA^{-1} if the motion is confined within the pores of the diameter of 5 nm, and up to a higher Q if the actual confinement volume is smaller). Our data indicate that the diameter of confinement volume in our system is no smaller than 1 nm, and therefore we do not probe the effects of confinement in the “ Q -perpendicular” geometry in the $Q < Q_C$ regime.

The residence time between jumps, τ_{res} , solely defines the HWHM of the Lorentzian broadening at high Q for a diffusion process with a distribution of jump lengths, whether in confined volume or not. Thus the fact that the QENS broadening at high Q is similar for both orientations demonstrates that the residence time is the same for the motions of benzene molecules in the directions parallel and perpendicular to the fibers axes. This justifies the assumption that we made using Eq. (2) regarding the character of the diffusion process

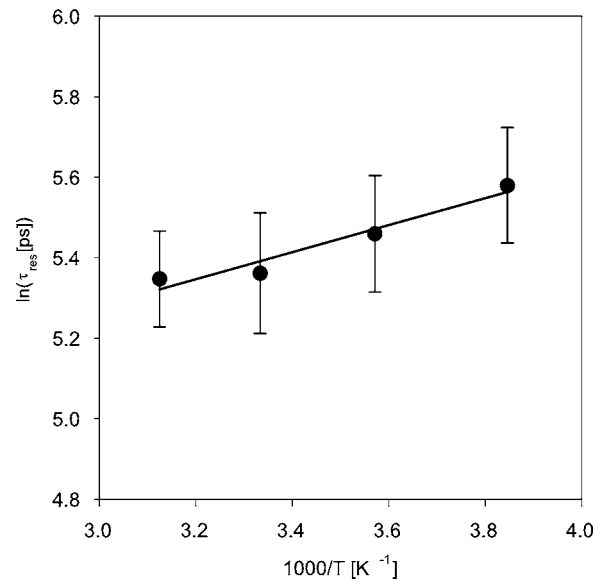


FIG. 6. The temperature dependence of the averaged residence time and its fit with Arrhenius law.

we observe, which can be considered as a three-dimensional diffusion process with a distribution of jump lengths. Since we have used an oriented rather than a powdered matrix, in the case of a one-dimensional diffusion process, when the diffusion jumps occur along the direction of the fibers axes, we would have observed no quasielastic broadening for the “ Q -perpendicular” orientation, whereas for the “ Q -parallel” orientation the Q dependence for the QENS broadening would be different from Eq. (2). The residence times for the “ Q -parallel” orientation determined from fitting the HWHM of the QENS broadening with Eq. (2) are shown in Table I. Also shown in Table I are the residence times for the “ Q -perpendicular” orientation determined from fitting the HWHM of the QENS broadening with a Q -independent constant \hbar/τ_{res} , which represents the high- Q limit of Eq. (2). While the residence times for the “ Q -parallel” orientation tend to be slightly shorter, the difference is within the experimental error, with the possible exception of the 320 K temperature point. Thus, the anisotropy of the benzene dynamics observed between the “ Q -perpendicular” and “ Q -parallel” orientations is either weak or negligible, as it should be for an isotropic three-dimensional diffusion process.

In principle, the rotational diffusion of benzene, that is, the reorientation of benzene molecules about their molecular sixfold symmetry axes perpendicular to the rings, also manifests itself in quasielastic signal. The corresponding QENS broadening takes the form of either one Lorentzian with Q -independent width in the model that allows jumps of an H atom from the current position to any of the other five available positions, or three Lorentzians with Q -independent widths in the more realistic model that restricts such jumps to the neighboring positions, thus allowing only $\pm 60^\circ$ orientation change in the course of a diffusion jump [11]. However, the residence time between such reorientational jumps is very short compared not only with the values of ≈ 200 – 300 ps observed in our experiment, but also with the

TABLE II. Parameters obtained from fitting the Q dependence of the Lorentzian half width at half maximum measured in the “ Q -parallel” geometry using Eq. (2). The diffusion coefficient was calculated from the fit parameters τ_{res} and $\langle r^2 \rangle$ as $D = \langle r^2 \rangle / 6\tau_{\text{res}}$. Standard deviation values are shown in parenthesis.

T (K)	$(\langle r^2 \rangle)^{1/2}$ (Å)	D (10^{-10} m ² /s)
320	3.1 (0.7)	0.88 (0.30)
300	3.9 (1.3)	1.31 (0.69)
280	3.8 (1.0)	1.00 (0.43)
260	3.6 (1.0)	0.92 (0.41)

entire dynamic range of the HFBS. Even for benzene molecules in direct contact with the pore walls in zeolites, the QENS measurements at room temperature have found the rotational diffusion residence times varying from 1–3 ps [4,12] to 16–32 ps [13]. In our experiment, because of a relatively large nanochannels diameter the majority of benzene molecules are in contact only with other benzene molecules in the bulklike phase. For bulk benzene, QENS experiments have measured the rotational diffusion residence time of ≈ 2.5 ps in the liquid phase at room temperature [14], and ≈ 20 ps in the solid phase just below the freezing point [11]. Since the confined benzene does not freeze in our experiment, and because a confinement in general tends to slow down dramatically the translational diffusion component, but has a much smaller effect on the rotational diffusion component, the rotational diffusion likely remains much faster than the dynamic range accessible in our experiment (about 20 ps) and just contributes to the background.

The fact that for the “ Q -perpendicular” orientation the QENS broadening does not decrease at low Q may suggest that the diffusion coefficient is larger in the directions perpendicular to the fibers axes, so the saturation value of \hbar/τ_{res} is reached at lower Q compared to the “ Q -parallel” orientation. With similar residence times between translational jumps, this would imply a larger diffusion jump length in the directions perpendicular to the fibers axes. An interesting idea is that the anisotropy in the QENS broadening observed at low Q might be indicative of preferred orientation of benzene molecules. For instance, if the molecules are oriented in such a way that their sixfold symmetry axes are parallel to the fibers axes, their reorientational jumps about the sixfold symmetry axes might contribute to the jump length assessable in the “ Q -perpendicular” geometry.

The temperature dependence of the averaged residence time is presented in Fig. 6. While the error bars are sufficiently large to draw a temperature-independent line through the data points, we attempted to fit the data with Arrhenius law. Interestingly, the residence time shows a very weak temperature dependence with the activation energy of just 2.8 ± 0.5 kJ/mol. This is a low value compared to the activa-

tion energy for the translational diffusion in liquid bulk benzene of 12–13 kJ/mol [15,16]. Strictly speaking, Fig. 6 shows the temperature dependence of the residence time between jumps rather than diffusion coefficient measured in Refs. [15,16]. However, the diffusion coefficient calculated from the residence time and the mean jump distance and shown in Table II is also almost temperature-independent within a margin of experimental error. The calculated diffusion coefficients are lower than bulk values measured at room temperature [15,16] by about an order of magnitude.

It should be noted that the data presented in Fig. 2 clearly suggest that the activation energy for the residence time between jumps for the confined benzene molecules is low because the quasielastic signal is present throughout the whole temperature range above ≈ 160 K. This indicates that at least up to 310 K (and probably up to much higher temperatures) the mobility of benzene does not increase sufficiently to make the QENS signal broader than the dynamic range of the experiment of ± 35 μeV .

IV. CONCLUSION

Our QENS study of the dynamics of benzene confined in the nanochannels of chrysotile asbestos fibers with a characteristic diameter of about 5 nm has demonstrated that liquid benzene does not freeze and exhibits translational mobility even below 200 K, until at about 160 K its dynamics becomes too slow for the μeV resolution of the neutron backscattering spectrometer. The residence time for the translational diffusion of the confined benzene obtained from fitting the QENS data collected in the temperature range of 260 K to 320 K shows a weak temperature dependence with the activation energy of 2.8 ± 0.5 kJ/mol, which is a small value compared to bulk benzene. For this temperature range, the residence time between jumps of about 200–300 ps has been measured, which is two orders of magnitude longer compared to bulk benzene. Having performed the measurements of the oriented sample with the scattering vector either parallel or perpendicular to the fibers axes, we have found virtually no anisotropy of the residence time between diffusion jumps. We conclude that the diffusive motion of benzene molecules confined in the nanochannels with a characteristic diameter of about 5 nm is isotropic.

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- [1] Y. Kumzerov and S. Vakhrushev, in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa (American Scientific Publishers, Los Angeles, 2004), Vol. 7, pp. 811–849.
- [2] E. Mamontov, Yu. A. Kumzerov, and S. B. Vakhrushev, *Phys. Rev. E* **71**, 061502 (2005).
- [3] A. Meyer, R. M. Dimeo, P. M. Gehring, and D. A. Neumann, *Rev. Sci. Instrum.* **74**, 2759 (2003).
- [4] H. Jobic, M. Bee, and A. Renouprez, *Surf. Sci.* **140**, 307 (1984).
- [5] H. Jobic, A. N. Fitch, and J. Combet, *J. Phys. Chem. B* **104**, 8491 (2000).
- [6] P. L. Hall and D. K. Ross, *Mol. Phys.* **42**, 673 (1981).
- [7] K. S. Singwi and A. Sjölander, *Phys. Rev.* **119**, 863 (1960).
- [8] P. A. Egelstaff, *An Introduction to the Liquid State* (Academic Press, London, 1967).
- [9] A. J. Dianoux, M. Pineri, and F. Volino, *Mol. Phys.* **46**, 129 (1982).
- [10] M. Bée, *Quasielastic Neutron Scattering* (Hilger, Bristol, 1988).
- [11] F. Fujara, W. Petry, W. Schnauss, and H. Sillescu, *J. Chem. Phys.* **89**, 1801 (1988).
- [12] H. Jobic, M. Bee, and A. J. Dianoux, *J. Chem. Soc., Faraday Trans. 1* **85**, 2525 (1989).
- [13] S. Mitra, A. K. Tripathy, N. M. Gupta, and R. Mukhopadhyay, *Appl. Phys. A: Mater. Sci. Process.* **74**, S1308 (2002).
- [14] D. J. Winfield and D. K. Ross, *Mol. Phys.* **24**, 753 (1972).
- [15] D. R. Falcone, D. C. Douglass, and D. W. McCall, *J. Phys. Chem.* **71**, 2754 (1967).
- [16] A. F. Collings and R. Mills, *J. Chem. Soc., Faraday Trans.* **66**, 2761 (1970).
- [17] <http://www.ncnr.nist.gov/dave>