Observation of a dynamic crossover in water confined in double-wall carbon nanotubes

X.-Q. Chu,[1] A. I. Kolesnikov,[2] A. P. Moravsky,[3] V. Garcia-Sakai,[4] and S.-H. Chen[1,*]

[1]*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[2]*Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[3]*MER Corporation, Tucson, Arizona 85706, USA*
[4]*NIST Center for Neutron Research, Gaithersburg, Maryland 20899-8562, USA*
and Department of Material Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
(Received 19 June 2007; published 22 August 2007)

High-resolution quasielastic neutron scattering spectroscopy was used to measure H_2O hydrated double-wall carbon nanotubes (DWNT). The measurements were made at a series of temperatures from 250 K down to 150 K. The relaxing-cage model was used to analyze the quasielastic spectra. We observed clear evidence of a fragile-to-strong dynamic crossover (FSC) at $T_L = 190$ K in the confined water. We further show that the mean-square atomic displacement of the hydrogen atoms in water exhibits a sharp change in slope at approximately the same temperature 190 K. Comparing the result with that obtained from the confined water in hydrophilic porous silica material MCM-41, we demonstrate experimentally that water confined in a hydrophobic substrate exhibits a lower dynamic crossover temperature by $\Delta T_L \approx 35$ K.

I. INTRODUCTION

Bulk water shows many anomalous behaviors, especially in the supercooled temperature range (below 0 °C): An anomalous increase of thermodynamic response functions and an apparent divergent behavior of transport coefficients toward a singular temperature $T_s = 228$ K [1]. To explain these anomalies it was proposed that supercooled water at ambient pressure consists of a mixture of a high (HDL) and a low (LDL) density water. At sufficiently low temperatures and higher pressures there is a first order phase transition line in the P-T plane separating the HDL from the LDL, the end point of which is the second (liquid-liquid) critical point of water (conjectured to be around $T_{C'} \approx 220$ K and $P \approx 1000$ bar [2]). With an increasing supercooling the structural relaxation time of water shows a steeper temperature dependence compared to that of the Arrhenius law. This behavior is known as a characteristics of a fragile liquid. It is known that many glass forming liquids exhibit the fragile behavior at moderately supercooled temperatures and then at sufficiently low temperature make a transition to a strong (Arrhenius) liquid. Water is supposed to have a glass transition temperature at $T_g = 165$ K [3]. Unfortunately for bulk water, the observation of the fragile to strong dynamic transition, as well as the experimental study of the water behavior around the second critical point are impossible due to intervention of the homogeneous nucleation phenomenon. It starts at $T_H = 235$ K, resulting in crystallization to form a hexagonal ice before it reaches the supercooled range of interest. It was predicted [4] that water should also show the transition to a strong liquid in this inaccessible temperature range, around $T_L = 228$ K.

Many theoretical simulations and experimental studies showed that the nucleation of water in nanometer size confinement can be strongly suppressed down to about T_g, thus opening an opportunity to study water behavior in this "no man's land" range. A series of quasielastic neutron scattering (QENS) experiments were performed recently on water in porous Vycor glass [5] and MCM-41-S materials, both having hydrophilic surfaces, with well calibrated pore size (50 Å in the case of Vycor glass and 10 to 18 Å in the case of MCM-41-S), where the freezing process of water was strongly inhibited down to 160 K [6–8]. It was clearly shown that water in these confinements exhibits a dynamic crossover from fragile to strong liquids at $T_L \approx 225$ K [8]. Recently, a series of neutron diffraction and NMR relaxation measurements on water/ice at a silica surface also demonstrate some kind of transition occurring at around 220 K [9]. MD simulations predict [10,11] that the porous materials with hydrophobic surface can further reduce T_L compared to water in hydrophilic confinement. One of these materials can be carbon nanotubes (CN).

Carbon nanotubes of nanometer diameter and micrometer length, besides many other interesting properties, can serve as a quasi-one-dimensional confinement for other materials. Due to hydrophobic interaction of water with carbon atoms CN can play a very important role in studying the properties of confined water. Owing to very weak van der Waals type interaction of water molecules with carbon [12] compared to a hydrogen bond interaction between water molecules, water confined in small diameter CN can be considered as quasi-one-dimensional water cluster.

Many MD simulations [13–24] and recently a few experimental studies [18,25–29] were dedicated to understand the structure and dynamics of water in single wall carbon nanotubes (SWNT). The behavior of water in small diameter SWNT cannot be continuously scaled by nanotube diameter. Water cannot enter SWNT at all for nanotubes of diameter smaller than 8 Å. Water in (6,6) SWNT (~ 8 Å diameter) can enter the nanotube as a small file (or chain) of water molecules and fast transfer through the nanotubes, as was shown by MD simulations [13]. Neutron scattering study of water in (10,10) SWNT (~ 14 Å diameter) revealed an anomalously

*Author to whom correspondence should be addressed. sowhsin@mit.edu

soft dynamics [18]. MD simulations [18,19] proposed the structure of the nanotube water at low temperatures as a square-ice sheet wrapped into a cylinder inside the SWNT and the interior water molecules in a chainlike configuration. A drastic decrease in hydrogen-bond connectivity of the central water-chain ($<$2) gives rise to anomalously enhanced thermal motions of water protons. For (9,9) SWNT with smaller diameter ($\sim$12 Å) there should be only the cylinder of water molecules inside nanotube [19], while for (12,12) SWNT of larger diameter ($\sim$16 Å) water at low temperatures assembles two interconnected cylinders (one into another) with continuous hydrogen bonded structure [20,21]. Thus water in nanotubes of 16 Å and larger diameter exhibits its more uniform structure.

Recent QENS experiments on water in SWNT of 14 Å diameter and in double wall carbon nanotubes (DWNT) of 16 Å inner diameter showed a fragile to strong liquid transition for water in SWNT at T_L=218 K, while only fragile behavior for water in DWNT in the temperature range studied down to 190 K [25]. In the present study, we extend QENS measurements on water in DWNT of 16 Å inner diameter to lower temperatures and show that water in this confinement exhibits the fragile to strong dynamic crossover at even lower temperature, 190 K.

II. SAMPLE PREPARATION AND QENS EXPERIMENT

The DWNT material was synthesized by the chemical vapor deposition technique. The subsequent purification with hydrochloric acid was followed by the oxidation of nontube carbon components in air at 300–600 °C. These preparation and purification steps produced micrometer-long nanotubes of a high purity, that is, with low metal catalyst content and low nontube carbon content. The nanotube ends were opened by exposing the purified material to air at 420 °C for about 30 min. The samples were characterized by transmission electron microscopy (TEM) and small-angle neutron diffraction. The (0,1) reflection of the two-dimensional hexagonal lattice of the bundle was evident in the diffraction data. The mean inner and outer diameters of the DWNT were 16±3 and 23±3 Å, respectively. The water absorption was controlled by the following procedure: A mixture of deionized water and the DWNT was equilibrated for 2 h in an enclosed volume at 110 °C; excess water was then evaporated at 35 °C until reaching the targeted water mass fraction. In the present work 3.2 g of DWNT sample was loaded with 12 wt. % of water. Hydrated nanotubes were placed in vacuum sealed thin annular aluminum sample holder chosen to ensure greater than 90% neutron beam transmission through the samples in order to minimize the effects due to multiple scattering. The sample was mounted onto the cold stage of a closed-cycle refrigerator, with the temperature being controlled within ±0.1 K. QENS experiments were performed using the high flux backscattering spectrometer [30] (HFBS) at the National Institute of Standards and Technology. The instrument was operated with a dynamic range of ±11 μeV, providing an energy resolution of 0.8 μeV, full width at half maximum. The measurements were performed

between 150 and 250 K in 10 K steps and at 5 K. The spectra obtained at 5 K were used as the resolution functions.

III. RELAXING CAGE MODEL ANALYSIS

The QENS measurement essentially gives the self-dynamic structure factor $S_H(Q,\omega)$ of the hydrogen atom in a typical water molecule convolved with the energy resolution function of the instrument. The $S_H(Q,\omega)$ is a Fourier transform of the intermediate scattering function (ISF) $F_H(Q,t)$ of the hydrogen atom of the water molecule confined in the DWNT. The Q-independent average translational relaxation time $\langle \tau_T \rangle$ is obtained from the QENS data by fitting them with the relaxing cage model (RCM) [31]. The RCM describes the translational dynamics of a typical water molecule at supercooled temperature in terms of the product of two functions:

$$F_H(Q,t) = F^S(Q,t)\exp[-(t/\tau_T(Q))^\beta], \qquad (1)$$

$$\tau_T(Q) \cong \tau_0(0.5Q)^{-\gamma}, \qquad (2)$$

where the first factor, $F^S(Q,t)$, represents the short-time vibrational dynamics of the water molecule in the cage of its neighbors. This short time intermediate scattering function is calculated in the Gaussian approximation using the known form of the density of states of the hydrogen atom in water [31]. This function is fairly insensitive to temperature variation, and thus can be calculated from an MD simulation. The second factor, the α-relaxation term, contains the stretch exponent β, and the Q-dependent translational relaxation time $\tau_T(Q)$, which is a strong function of temperature. The latter quantity is further specified by two phenomenological parameters τ_0 and γ, the prefactor and the exponent controlling the power-law Q dependence of $\tau_T(Q)$, respectively. The average translational relaxation time, which is a Q-independent quantity we use in this paper, is defined as $\langle \tau_T \rangle = \tau_0 \Gamma(1/\beta)/\beta$, where $\Gamma(x)$ is the gamma function. The temperature dependence of the translational relaxation time is calculated from three fitted parameters, τ_0, β, and γ, by analyzing a group of quasielastic peaks at different Q values simultaneously. For this analysis, we chose seven spectra from data taken at HFBS at each temperature, as described in detail in Ref. [32].

IV. RESULTS AND DISCUSSIONS

Figure 1 shows qualitatively that there is some kind of crossover temperature at around 190 K visible from the inspection of temperature variation of the quasielastic peak height and width. However, a much sharper definition of this dynamic crossover temperature T_L can be obtained from the RCM analysis of the normalized quasielastic peak.

Figure 2 illustrates the degree of agreement of RCM with the measured QENS data. The comparison was made of the data taken from temperatures just above and below the crossover temperature T_L.
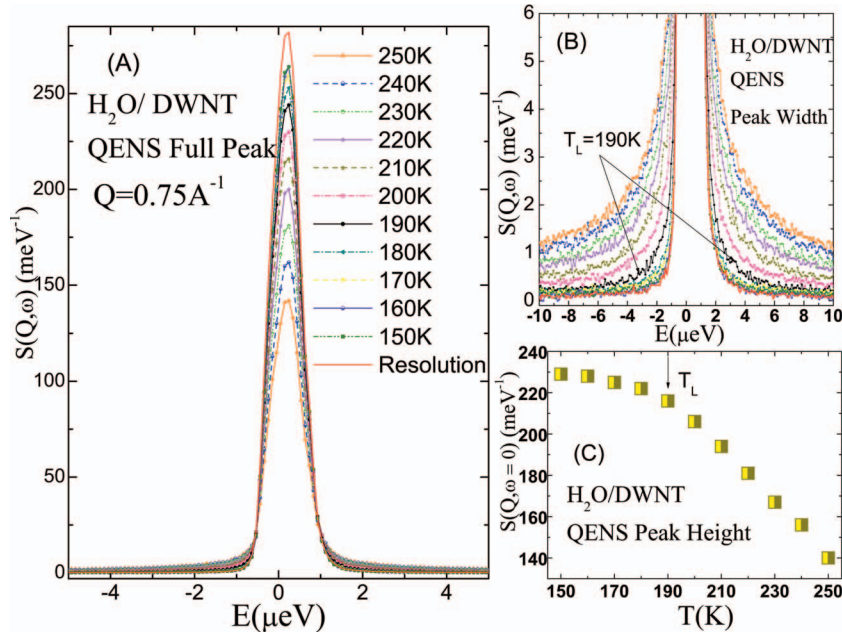
FIG. 1. (Color online) Measured QENS spectra at various temperatures T. (A) Normalized QENS spectra at $Q=0.75$ Å^{-1}. (B) Wings of the peaks, from which we extract the average relaxation time $\langle\tau_T\rangle$ by fitting with RCM. (C) T dependence of the peak heights, which is related to the MSD of the H atoms of the confined water through the Debye-Waller factor. Both peak widths and peak heights indicate qualitatively the existence of a crossover temperature T_L for the confined water.

Figure 3 compares the log $\langle\tau_T\rangle$ vs $1/T$ plots of water confined in two different materials, DWNT and MCM-41. In (A), at temperatures above 190 K, $\langle\tau_T\rangle$ obeys a Vogel-Fulcher-Tammann (VFT) law, namely, $\langle\tau_T\rangle=\tau_0\exp[DT_0/(T-T_0)]$, where D is a dimensionless parameter providing the measure of fragility and T_0 is the ideal glass transition temperature. Below 190 K, the $\langle\tau_T\rangle$ switches over to an Arrhenius behavior, which is $\langle\tau_T\rangle=\tau_0\exp(E_A/RT)$, where E_A, is the
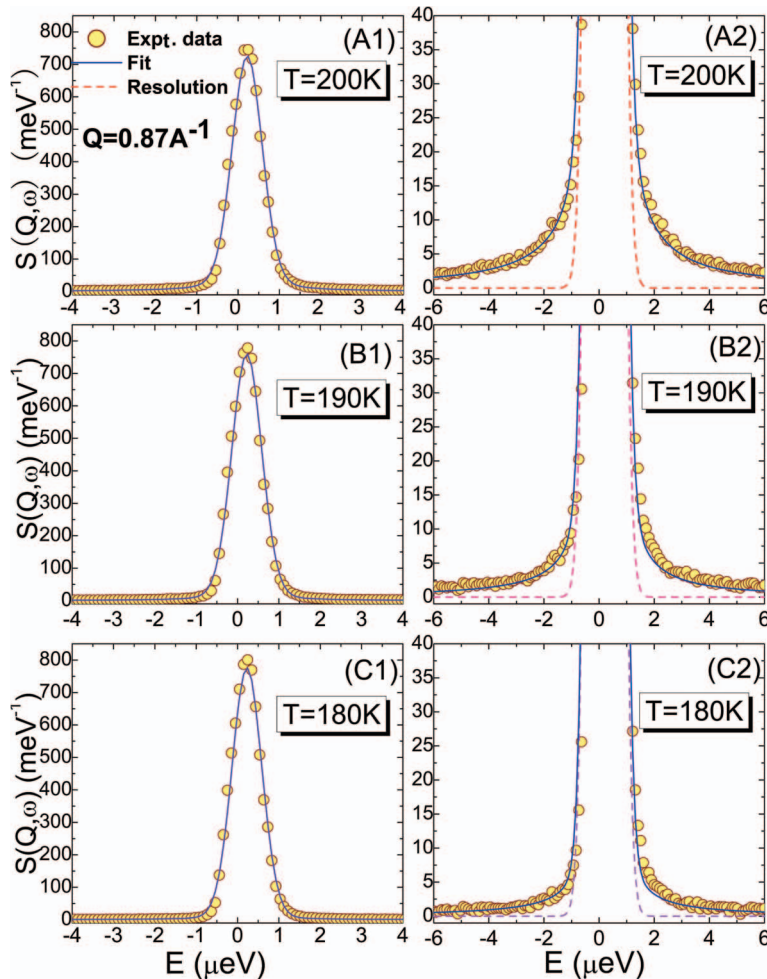

FIG. 2. (Color online) RCM analyses of QENS experimental data. We show the result in three different temperatures: $T=200$ K [above T_L, (A1) and (A2)]; $T=190$ K [at T_L, (B1) and (B2)]; and $T=180$ K [below T_L, (C1) and (C2)]. The panels on the left-hand side show the fitted curves (solid lines) of the full peak. The panels on the right-hand side show the comparison of the fitted curves (solid lines) with the data on the wing of the peak together with the resolution functions (dash lines). We can see the broadening of the quasielastic wings become smaller when temperature decreases.
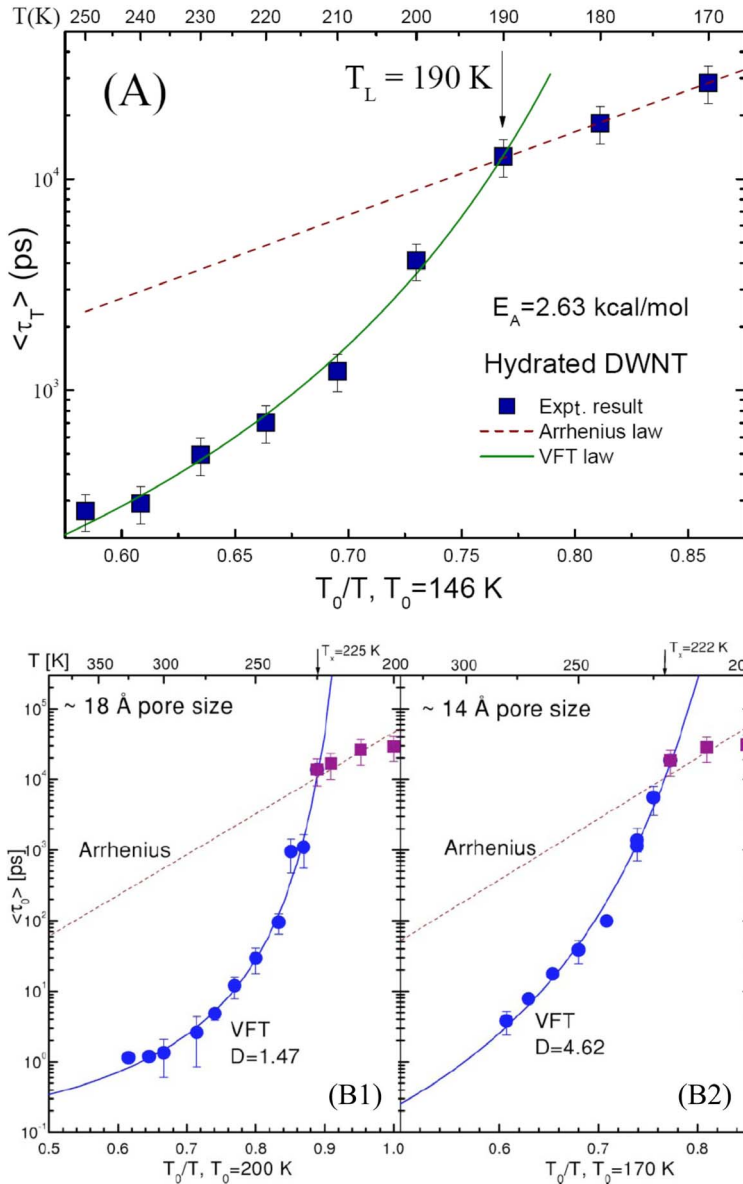
FIG. 3. (Color online) (A) Extracted average translational relaxation time $\langle \tau_T \rangle$ from fitting of the quasielastic spectra of water confined in DWNT (inner diameter 16 Å) by RCM plotted in a log scale against $1/T$. It shows a well-defined cusplike dynamic crossover behavior occurring at $T_L = 190$ K. The solid line represents fitted curves using the VFT law, while the dashed line is the fitting according to the Arrhenius law. For comparison, (B1) and (B2) show the results of our previous experiments on supercooled water confined in porous silica material MCM-41 with two different pore sizes, which show that the crossover temperature TL is insensitive to confinement pore sizes. From the results shown in the upper and lower panels, we estimate that the water confined in a hydrophobic substrate (DWNT) has a lower dynamic crossover temperature by $\Delta T_L \approx 35$ K, as compared to that in a hydrophilic substrate (MCM-41).

activation energy for the relaxation process and R is the gas constant. This dynamic crossover from the super-Arrhenius (the VFT law) to the Arrhenius behaviors is cusplike and thus it sharply defines the crossover temperature to be $T_L = 190$ K, much more accurately than that indicated by temperature variation of the peak heights and peak widths, shown in Fig. 1. In (B1) and (B2) we show the same analyses of water confined in MCM-41 with two different pore sizes previously published for comparison [5]. Note that the crossover temperature in the case of MCM-41 is 224 ± 2 K.

Figure 4 shows the mean-squared atomic displacement (MSD) of the confined water molecule, $\langle x_{H_2O}^2 \rangle$, in the observational time interval of about 2 ns (corresponding to the energy resolution of 0.8 μeV). One can detect a dynamic crossover phenomenon in terms of the sudden change of the slope at around 190 K, in agreement with the Arrhenius plot of the relaxation time in Fig. 3(a). Note, however, that MSD

vs T plot cannot define a sharp crossover temperature as the relaxation time plot.

V. CONCLUSIONS

As one can observe from Fig. 3, the crossover temperature for water confined in a hydrophilic substrate (MCM-41) is higher than that confined in a hydrophobic substrate (DWNT) by about 35 K. Previously we detect the crossover temperatures in hydrated DNA to be 222 K [33], vs in the case of protein lysozyme to be 220 K [32], showing that DNA has more hydrophilic interface presumably due to the presence of the phosphate groups. Thus it can be conjecture that the magnitude of the crossover temperature T_L can be used as an indicator of the hydrophilisity of the substrate. A good test of this idea may be to measure the crossover temperatures of protein hydration water with proteins of different hydrophilic and hydrophobic interfacial exposure.
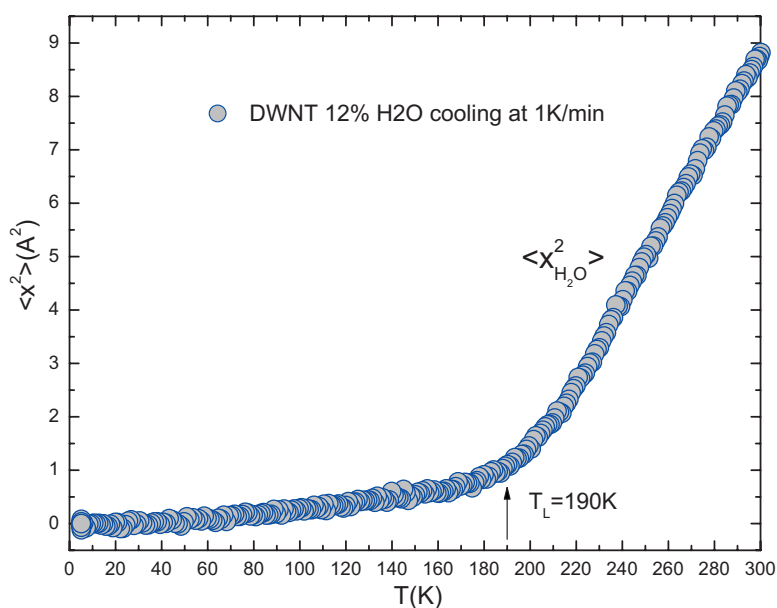
FIG. 4. (Color online) Mean-squared atomic displacement (MSD) averaged over all the hydrogen atoms, $\langle x^2 \rangle$, extracted from the Debye-Waller factor measured by an elastic scan with resolution of 0.8 μeV, as a function of temperature for the H_2O confined in DWNT. One can clearly see a sharp transition of slope at around 190 K, indicating the approximate location of the dynamic crossover temperature.

[1] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).
[2] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
[3] V. Velikov, S. Borick, and C. A. Angell, Science **294**, 2335 (2001).
[4] K. Ito *et al.*, Nature (London) **398**, 492 (1999).
[5] J.-M. Zanotti, M.-C.M.-C. Bellissent-Funel, and S.-H. Chen, Europhys. Lett. **71**, 91 (2005).
[6] A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, J. Chem. Phys. **121**, 10843 (2004).
[7] L. Liu, S.-H. Chen, A. Faraone, C.-W Yen, and C.-Y. Mou, Phys. Rev. Lett. **95**, 117802 (2005).
[8] L. Liu, S.-H. Chen, A. Faraone, C.-W Yen, C.-Y. Mou, A. I. Kolesnikov, E. Mamontov and J. Leao, J. Phys.: Condens. Matter **18**, S2261 (2006).
[9] E. Liu, J. C. Dore, J. B. W. Webber, D. Khushalani, S. Jähnert, G. H. Findenegg, and T. Hansen, J. Phys.: Condens. Matter **18**, 10009 (2006).
[10] I. Brovchenko and A. Oleinikova, J. Chem. Phys. **126**, 214701 (2007).
[11] P. Kumar, S. V. Buldyrev, F. W. Starr, N. Giovambattista, and H. E. Stanley, Phys. Rev. E **72**, 051503 (2005).
[12] J. H. Walter, R. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Phys. Chem. B **105**, 9980 (2001).
[13] G. Hummer, J. C. Rasalaiah, and J. P. Noworyta, Nature (London) **414**, 188 (2001).
[14] K. Koga, G. T. Gao, H. Tanaka, and X. C. Zeng, Nature (London) **412**, 802 (2001).
[15] W. H. Noon, K. D. Ausman, R. E. Smalley, and J. Ma, Chem. Phys. Lett. **355**, 445 (2002).
[16] J. Martí and M. C. Gordillo, Phys. Rev. B **63**, 165430 (2001).
[17] J. Martí and M. C. Gordillo, Phys. Rev. E **64**, 021504 (2001).
[18] A. I. Kolesnikov, J.-M. Zanotti, C.-K. Loong, P. Thiyagarajan, A. P. Moravsky, R. O. Loutfy, and C. J. Burnham, Phys. Rev. Lett. **93**, 035503 (2004).
[19] A. I. Kolesnikov, C.-K. Loong, N. R. de Souza, C. J. Burnham, and A. P. Moravsky, Physica B **385**, 272 (2006).
[20] A. Striolo, A. A. Chiavlvo, K. E. Gubbins, P. T. Cummings, J. Chem. Phys. **122**, 234712 (2005).
[21] J. Bai and X. C. Zeng, Proc. Natl. Acad. Sci. U.S.A. **103**, 19664 (2006).
[22] I. Hanasaki and A. Nakatani, J. Chem. Phys. **124**, 174714 (2006).
[23] B. K. Agrawal, V. Singh, A. Pathak, and R. Srivastava, Phys. Rev. B **75**, 195420 (2007).
[24] T. Kurita, S. Okada, and A. Oshiyama, Phys. Rev. B **75**, 205424 (2007).
[25] E. Mamontov, C. J. Burnham, S.-H. Chen, A. P. Moravsky, C.-K. Loong, N. R. de Souza, and A. I. Kolesnikov, J. Chem. Phys. **124**, 194703 (2006).
[26] Y. Maniwa, H. Kataura, M. Abe, S. Suzuki, Y. Achiba, H. Kira, and K. Matsuda, J. Phys. Soc. Jpn. **71**, 2863 (2002).
[27] K. Matsuda, T. Hibi, H. Kadowaki, H. Kataura, and Y. Maniwa, Phys. Rev. B **74**, 073415 (2006).
[28] G. Reiter, C. Burnham, D. Homouz, P. M. Platzman, J. Mayers, T. Abdul-Redah, A. P. Moravsky, J. C. Li, C.-K. Loong, A.

I. Kolesnikov, Phys. Rev. Lett. **97**, 247801 (2006).

[29] O. Byl, J.-C. Liu, Y. Wang, W.-L. Yim, J. K. Johnson, and J. T. Yates Jr., J. Am. Chem. Soc. **128**, 12090 (2006).

[30] A. Meyer, R. M. Dimeo, P. M. Gehring, and D. A. Neumann, Rev. Sci. Instrum. **74**, 2759 (2003).

[31] S.-H. Chen, C. Liao, F. Sciortino, P. Gallo, and P. Tartaglia, Phys. Rev. E **59**, 6708 (1999).

[32] S.-H. Chen, L. Liu, E. Fratini, P. Baglioni, A. Faraone, and E. Mamontov, Proc. Natl. Acad. Sci. U.S.A. **103**, 9012 (2006).

[33] S.-H. Chen, L. Liu, X. Chu, Y. Zhang, E. Fratini, P. Baglioni, A. Faraone, and E. Mamontov, J. Chem. Phys. **125**, 171103-1-4 (2006).