Layering of confined water between two graphene sheets and its liquid–liquid transition*

Xuyan Zhou(周戌燕), Yunrui Duan(段云瑞), Long Wang(王龙), Sida Liu(刘思达), Tao Li(李涛), Yifan Li(李一凡), and Hui Li(李辉)†

Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Ji'nan 250061, *China*

(Received 13 June 2017; revised manuscript received 22 July 2017; published online 10 September 2017)

Molecular dynamics (MD) simulations are performed to explore the layering structure and liquid–liquid transition of liquid water confined between two graphene sheets with a varied distance at different pressures. Both the size of nanoslit and pressure could cause the layering and liquid–liquid transition of the confined water. With increase of pressure and the nanoslit's size, the confined water could have a more obvious layering. In addition, the neighboring water molecules firstly form chain structure, then will transform into square structure, and finally become triangle with increase of pressure. These results throw light on layering and liquid–liquid transition of water confined between two graphene sheets.

Keywords: confined water, layering, liquid–liquid transition

PACS: 64.70.Ja, 64.70.Nd, 64.70.pm **DOI:** 10.1088/1674-1056/26/10/106401

1. Introduction

Water, the fountainhead of the cosmic inventory, is not only so indispensable to all living creatures that it renders its involvement in a vast number of processes which has important relevance to the survival of every organism such as respiration and the transportation of nutrients and metabolite, but also a topic perpetual interest due to its remarkable anomalous properties and important implications to natural science,[1] biological science,[2–6] material science,[7–11] etc. The bulk water has various solid structures including more than 15 crystalline phases and 3 amorphous phases. Because of the existence of rock, cell, microemulsion, ionic channel and interstellar, water is usually confined in many real situations, attracting a lot of attention devoted to structural and dynamical properties of water in restricted geometries.[12,13]

In the 1980s, Mishima *et al.*[14,15] adopted the experimental technique to reveal that a sudden change would happen between two amorphous phases of water and Poole *et al.*[16] via computer simulation forecast that liquid water might exist in a various of forms. Then, the transition between multiphase structures of the same liquid has attracted a keen interest. Recently, existing theories and present studies have confirmed that liquid–liquid transition could take place in supercooled water under certain conditions.[17] Up to now, liquid–liquid transition of supercooled water is usually caused by two factors: temperature and pressure.[18] Plenty of researches[19,20] have demonstrated that the supercooled water has a low-density liquid phase. Huang *et al.*[21] used small-angle x-ray scattering to verify the presence of density fluctuations in ambient water; this is retained with decreasing temperature while the magnitude is enhanced. Soper and Ricci[22] revealed that supercooled water has two different structures and both density and structure will change during the liquid–liquid transition. To sum up, previous studies almost focus on the liquid–liquid transition of supercooled water,[23,24] very few attention is paid to the liquid–liquid transition of the confined water.

During the last decade, simulations and experiments have been performed to study the water confined in various confined substrates, which have evidenced for confined water a rich variety of thermodynamics phenomena more puzzling than those known for bulk water.[25,26] In addition, phase behavior of water in confined space could be dramatically influenced by several factors, such as density,[27] pressure,[28,29] temperature,[30] and size of the confinedment.[31–33] Until now, despite plenty of progresses from both experimental techniques[34,35] and analytical theories[36–41] has been made in exploring the complex structures of water, it is still necessary to further probe it.

Here, we used MD simulation to explore the layering and liquid–liquid transition of confined water in nanoslit.

2. Models and theoretical methods

In this work, we employ MD simulation to investigate the structural evolution of water confined between two graphene sheets with a distance ranging from 8 Å to 14 Å (as shown in Fig. 1). The normal of the two graphene sheets is in the z direction. The periodic boundary conditions are applied to directions parallel to graphene sheets and the size of the original simulation box is 80.990 Å×80.990 Å×100 Å.

*Project supported by the National Natural Science Foundation of China (Grant No. 51271100), the National Key Research Program of China (Grant No. 2016YFB0300501), and the Taishan Scholar Construction Engineering.

†Corresponding author. E-mail: lihuilmy@hotmail.com

© 2017 Chinese Physical Society and IOP Publishing Ltd

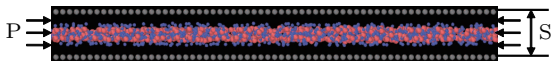


Fig. 1. (color online) The initial model of simulation system. Red: oxygen atoms; blue: hydrogen atoms; gray: carbon atoms.

All MD calculations are carried out by the package LAMMPS[42] in the constant number, pressure and temperature (NPT) ensemble, where the temperature is controlled by a Nose–Hoover thermostat. The interaction among water is described by the four-point TIP4P[43] rigid model. The SHAKE algorithm[44] is adopted to restrict the H–O distance and H–O–H angle. The adaptive intermolecular reactive empirical bond order (AIREBO) potential[45] is adopted to model the C–C interaction, and the interaction between water and carbon is described by the Lennard–Jones (LJ) potentail. The water molecules also interact via the LJ potential. The velocity Verlet algorithm[46] with a time step of 1.0 fs is chosen to calculate the time integration of Newton's equation of the motion. We exert the constant pressure on water molecules, and the pressure is parallel to two graphene sheets varied from 0.505 GPa to 30.3 GPa. Moreover, all simulations are performed at a temperature of 300 K for 1 ns. To improve the computational efficiency, the substrates are fixed during the simulation process.

3. Results and discussion

First, we explore the layering structure of confined water in various nanoslits. Figure 2 gives the final structures confined between two graphene sheets with a distance ranging from 8 Å to 14 Å at various pressures ranging from 0.505 GPa to 30.3 GPa. It can be seen that at the beginning of the simulation, all the water molecules are stacked disorderly, while once water molecules contact with substrates, water molecules adjacent to two graphene sheets immediately form two ordered liquid layers. This phenomenon has been confirmed by both analytical theories[47] and experimental techniques,[48] suggesting that when a liquid comes into contact with a solid wall, the liquid atoms or molecules will be layered adjacent to the wall, giving rise to an oscillatory density profile. After relaxing at 300 K all water molecules are layered along z direction to form an order structure although the relaxing temperature is much higher than the melting point of water. Importantly, both pressure and the distance between two sheets have a dramatic effect on layering of the final structure. For the size of 8.0, 12.0 or 14.0 Å, although the pressure changes, the final structure has the constant layers corresponding to the nanoslit. However, for the size of 10 Å, the final structure gradually turns two layers into three layers at the pressure of 30.3 GPa with increase of pressure, meaning the occurrence of liquid–liquid transition because the change of layer could be regarded as an expression of the liquid–liquid transition.[49] In addition, before the layer transformation, the distance of water layers will be enlarged with the increase of pressure, while the effect of pressure will decrease in a wide nanoslit. For the same pressure, an increasing distance will also affect layering. For example, at a pressure of 10.1 GPa, water molecules would be divided into two layers at the distance of 8 Å, while when distance is 12 Å, three layers would be observed. Further increasing the nanoslit size, water molecules in final structure will be divided into four layers at 14 Å. To sum up, the layers increase with increase of pressure or the nanoslit's size, that is to say, both pressure and the nanoslit's size could induce the liquid–liquid transition.

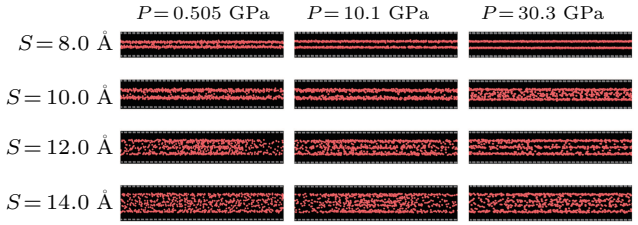


Fig. 2. (color online) Snapshots of liquid water with constant atoms between two graphene sheets with a distance ranging from 8 Å to 14 Å at various pressures ranging from 0.505 GPa to 30.3 GPa.

Density distribution functions (DDFs) are plotted to further explore the combined effect of pressure and the distance of two graphene sheets on stratification phenomenon. For convenience, we consider the position of oxygen atom as the core of water molecule. Figures 3(a)–3(d) give the DDFs of water molecules in different cases to explore the influence of these two factors. For the distance of 8 Å, every final structure is constituted by two layers of water molecule, shown in DDF curves as two isolated peaks with the same intensity. When the nanoslit size reaches 10 Å, there are still only two dispersed peaks at a lower pressure, while at a higher pressure of 20.2 GPa, the arrow mark in line exists two little peaks. Then with pressure increasing to 30.3 GPa, these two little peaks gradually advance towards the middle and are combined into one peak, resulting in three discrete density peaks observed, declaring that higher pressure can cause an obvious layer phenomenon, further giving rise to a structural transformation. When the nanoslit's size reaches 12 Å, three dispersed peaks appear in all DDF curves. For the distance of 14 Å, four dispersed peaks exist in all cases. Besides, with increase of the size, the peaks on two sides become farther and farther, exhibiting that at size of 8 Å, all the distances between two density peaks are about 2 Å, which is much closer than that (about 7 Å) at the size of 14 Å. What is more, in the same nanoslit, a higher pressure can lead to a more obvious stratification phenomenon, but the effect of pressure on stratification phenomenon becomes weaker with the size of nanoslit increasing. In addition, as for the system with more than two layers, the intensity of two density peaks on two sides is much higher than the peak(s) in the middle position.

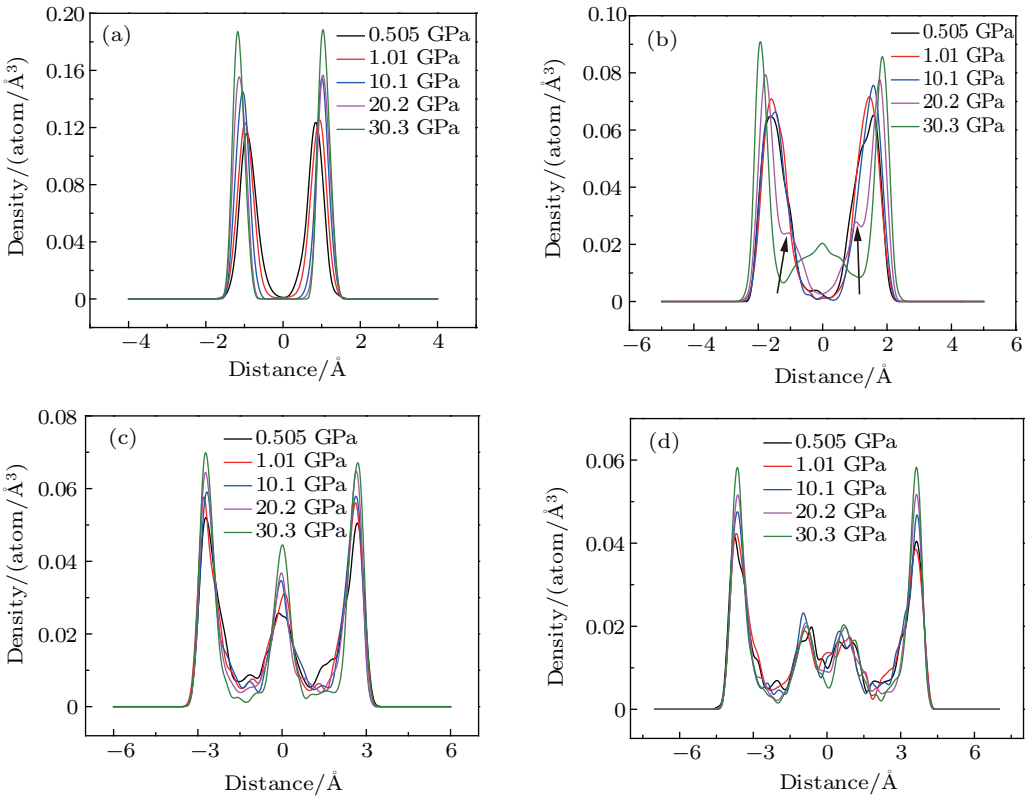


Fig. 3. (color online) The DDFs of water molecules along z direction in different cases: (a) 8.0 Å; (b) 10.0 Å; (c) 12.0 Å; (d) 14.0 Å.

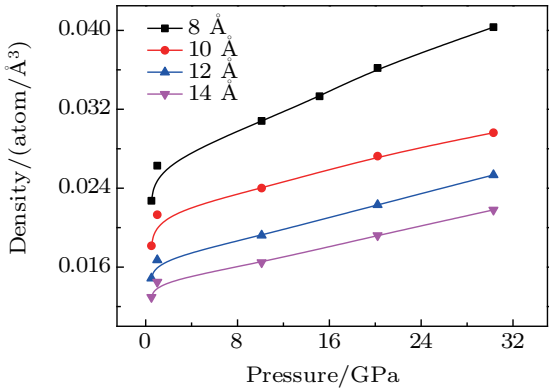


Fig. 4. (color online) Average density of the confined water at different pressures.

Average density curves of these systems with change of pressure are shown in Fig. 4. As pressure increases, an uneven variation appears in every density curve and the density of final structure gradually increases, which means the water molecules stack more and more closely with the increase of pressure. For the same pressure, with distance increasing, water molecules are loosely arranged, exhibiting that the density of the final structure gradually decreases. Notably, with the increase of pressure, the rise of the density is different and a bigger rise appears in a narrower slit, implying that the density of water molecules is more sensitive to pressure in a narrow slit. It is worth while mentioning that another expression of the liquid–liquid transition is the density change of the system. From previous discussions, both pressure and nanoslit's size could lead to the change of the density, implying that these two factors could cause the liquid–liquid transition.

From the previous section, the pressure affects the laying of confined water significantly. It is necessary to discuss whether pressure has an influence on inner structure of every layer. As for the liquid water confined between two graphene sheets with a distance of 8 Å, water molecules are divided into two layers along the z direction in all cases. Figure 5 shows the final structures of water molecules in one layer at a pressure range from 0.505 GPa to 30.3 GPa. It can be seen that the pressure has an obvious effect on the final structure and that water molecules are stacked based on different structures with pressure increasing. For a low pressure, such as 0.505 GPa, water molecules are stacked in a line to form a chainlike structure. With increase of the pressure, some four neighboring water molecules will occupy the four corner positions of square and exhibit a square structural unit at the pressure of 1.01 GPa. When the pressure increase to 10.1 GPa, there is no chainlike structures in the final structure. At 15.15 GPa, most of water molecules are stacked based on square to form a more regular square structure. When the pressure reaches 20.2 GPa, water molecules are stacked more closely and even some neighboring molecules forms a triangle structure unit. At 30.3 GPa, all the three neighboring water molecules oc-

cupy the three corners of triangle and an ideal triangle structure would be observed. To sum up, with the increase of pressure, the stacked pattern of water molecules is chain firstly, then becomes square and finally gradually transforms to triangle.

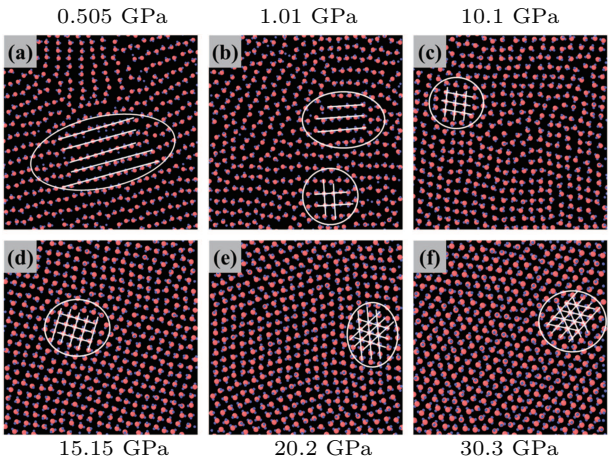


Fig. 5. (color online) Snapshots of water molecules in one layer between two graphene sheets with a distance of 8 Å at various pressures ranging from 0.505 GPa to 30.3 GPa.

It is found that the distance between two layers is not the same at different pressures, so DDFs are plotted to explore the influence of pressure on the distance of the two water layers. Figure 6 gives the DDFs of the bilayer system at different pressures ranging from 0.505 GPa to 30.3 GPa. It can be seen that whatever pressure is, every DDF of the system exhibits four discrete and symmetric peaks. The peaks on the two sides, standing for two graphene sheets, have a higher intensity than that on behalf of water molecules in the middle. Moreover, peaks of two graphene sheets have the same intensity and position, which is quite different from the peaks of water molecules, exhibiting that both position and intensity change. When pressure is 0.505 GPa, the distance between the two middle peaks is about 1.8 Å, much less than that (about 2.2 Å) at the pressure of 30.3 GPa. That is to say, with the increase of pressure, the distance between two density peaks of water molecules increases and the two peaks gradually move away from each other. At the same time, the intensity of the density peaks becomes higher and higher as pressure increases, indicating that the higher pressure can lead to a more obvious stratification phenomenon.

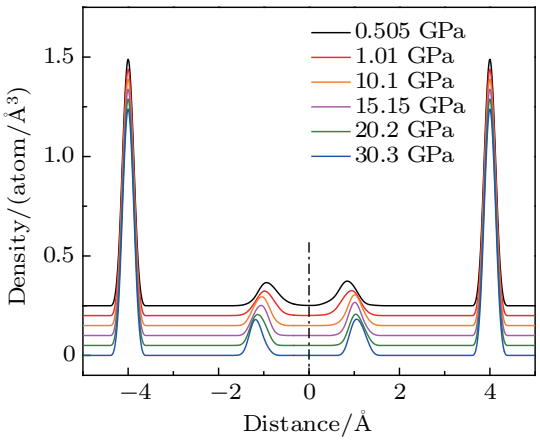


Fig. 6. (color online) Density distribution functions (DDFs) of water molecules along z direction at different pressure ranging from 0.505 GPa to 30.3 GPa.

Figures 7(a)–7(c) give the bond angle distributions (BADs) of the bilayer system at different pressures ranging from 0.505 GPa to 30.3 GPa, respectively. Insets in Figs. 6(a)–7(c) aim at explaining the bond angle distribution. When the pressure is 0.505 GPa, only one peak appears about at the angle of 180°. The inset in Fig. 7(a) shows the stacking pattern among water molecules, so we can know that water molecules are stacked based on a chain. As pressure increases to 15.15 GPa, there are two peaks at 90° and 180°, separately. From the inset, these two peaks in BAD curve stand for a square structure. As for the pressure of 30.3 GPa, the curve exhibits three discrete peaks at 60°, 120°, and 180°, indicating that every three molecules occupy the three angles of triangle to form a triangular structure. Now, the density of the final structure is the highest among these three structures. In general, different pressures correspond to the specific stacking pattern of water molecules and with the increase of pressure from 0.505 GPa to 30.3 GPa, the stacking pattern varies from chain, square to triangle.

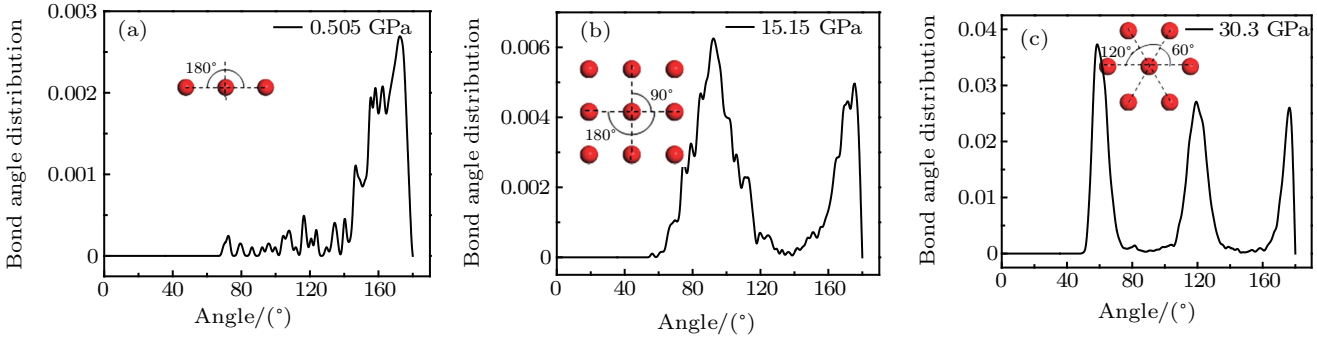


Fig. 7. (color online) Bond angle distributions (BADs) of the bilayer system at pressures 0.505 GPa (a), 15.15 GPa (b), and 30.3 GPa (c), respectively. Insets in panels (a)–(c) aim at explaining the bond angle distribution.

4. Conclusion

This study systematically investigates the layer structure and liquid–liquid transition of water confined between two graphene sheets by MD simulation. Not only the pressure but also the size of nanoslit could induce liquid–liquid transition, behaved as the change of layering, as well as the change of stacking pattern of water molecules in every layer. With increase of pressure and the nanoslit's size, the layering in confined water becomes more and more obvious. Furthermore, by changing pressure, three structures of water confined between two graphene sheets are obtained. With increase of pressure, they firstly form chain structure, then transform into square structure, and finally become triangle. These findings could provide an opportunity for comprehensive understanding of layering and liquid–liquid transition of water in confined nanoslit.

References

[1] Brown G E 2001 *Science* **294** 67
[2] Zangi R 2004 *J. Phys.: Condens. Matter* **16** S5371
[3] Pratt L R and Pohorille A 2002 *Chem. Rev.* **102** 2671
[4] Sansom M S P and Biggin P C 2001 *Nature* **414** 156
[5] Tajkhorshid E, Nollert P, Jensen M Ø, Miercke L J, O'Connell J, Stroud R M and Schulten K 2002 *Science* **296** 525
[6] Lu X, Shi R, Hao C, Chen H, Zhang L, Li J, Xu G and Sun R 2016 *Chin. Phys. B* **25** 090506
[7] Ren H, Li X, Li H, Zhang L and Wu W 2015 *Phys. Chem. Chem. Phys.* **17** 11284
[8] Ren H, Zhang L, Li X, Li Y, Wu W and Li H 2015 *Phys. Chem. Chem. Phys.* **17** 23460
[9] Gao X, Wang Q, Sun G, Li C X and Hu L 2016 *Chin. Phys. B* **25** 026801
[10] Yi Z, Deng P N, Zhang L L and Li H 2016 *Chin. Phys. B* **25** 106401
[11] Shao W H and Chen W Z 2015 *Chin. Phys. B* **24** 054701
[12] Bellissent-Funel M C 2001 *J. Phys.: Condens. Matter* **13** 9165
[13] Kumar P, Buldyrev S V, Starr F W, Giovambattista N and Stanley H E 2005 *Phys. Rev. E* **72** 051503
[14] Mishima O, Calvert L D and Whalley E 1985 *Nature* **314** 76
[15] Mishima O 1994 *J. Chem. Phys.* **100** 5910
[16] Poole P H, Sciortino F, Essmann U and Stanley H E 1992 *Nature* **360** 324
[17] Palmer J C, Martelli F, Liu Y, Car R, Panagiotopoulos A Z and Debenedetti P G 2014 *Nature* **510** 385
[18] Mishima O and Stanley H E 1998 *Nature* **392** 164
[19] Poole P H, Becker S R, Sciortino F and Starr F W 2011 *J. Phys. Chem. B* **115** 14176
[20] Mallamace F, Broccio M, Corsaro C, Faraone A, Majolino D, Venuti V, Liu L, Mou C Y and Chen S H 2007 *Proc. Natl. Acad. Sci. USA* **104** 424
[21] Huang C, Wikfeldt K T, Tokushima T, Nordlund D, Harada Y, Bergmann U, Niebuhr M, Weiss T M, Horikawa Y, Leetmaa M, Ljungberg M P, Takahashi O, Lenz A, Ojamäe L, Lyubartsev A P, Shin S, Pettersson L G M and Nilsson A 2009 *Proc. Natl. Acad. Sci. USA* **106** 15214
[22] Soper A K and Ricci M A 2000 *Phys. Rev. Lett.* **84** 2881
[23] Brovchenko I, Geiger A and Oleinikova A 2005 *J. Chem. Phys.* **123** 044515
[24] Meyer M and Stanley H E 1999 *J. Phys. Chem. B* **103** 9728
[25] Ricci M A, Bruni F, Gallo P, Rovere M and Soper A K 2000 *J. Phys.: Condens. Matter* **12** A345
[26] Truskett T M, Debenedetti P G and Torquato S 2001 *J. Chem. Phys.* **114** 2401
[27] Qiu H, Zeng X C and Guo W 2015 *ACS Nano* **9** 9877
[28] Giovambattista N, Rossky P J and Debenedetti P G 2006 *Phys. Rev. E* **73** 041604
[29] Bai J and Zeng X C 2012 *Proc. Natl. Acad. Sci. USA* **109** 21240
[30] Koga K, Tanaka H and Zeng X C 2000 *Nature* **408** 564
[31] Zangi R and Mark A E 2003 *Phys. Rev. Lett.* **91** 025502
[32] Kaneko T, Bai J, Yasuoka K, Mitsutake A and Zeng X C 2014 *J. Chem. Phys.* **140** 184507
[33] Zhu Y, Wang F, Bai J, Zeng X C and Wu H 2015 *ACS Nano* **9** 12197
[34] Jinesh K B and Frenken J W M 2008 *Phys. Rev. Lett.* **101** 036101
[35] Faraone A, Liu L, Mou C Y, Yen C W and Chen S H 2004 *J. Chem. Phys.* **121** 10843
[36] Gallo P, Ricci M A and Rovere M 2002 *J. Chem. Phys.* **116** 342
[37] Hanasaki I and Nakatani A 2006 *J. Chem. Phys.* **124** 174714
[38] Gordillo M C and Martı J 2000 *Chem. Phys. Lett.* **329** 341
[39] Bai J, Angell C A and Zeng X C 2010 *Proc. Natl. Acad. Sci. USA* **107** 5718
[40] Zangi R and Mark A E 2003 *J. Chem. Phys.* **119** 1694
[41] Giovambattista N, Rossky P J and Debenedetti P G 2009 *Phys. Rev. Lett.* **102** 050603
[42] Fowlkes J D, Kondic L, Diez J, Wu Y and Rack P D 2011 *Nano Lett.* **11** 2478
[43] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 *J. Chem. Phys.* **79** 926
[44] Krätler V, Van Gunsteren W F and Hünenberger P H 2001 *J. Comput. Phys.* **22** 501
[45] Stuart S J, Tutein A B and Harrison J A 2000 *J. Chem. Phys.* **112** 6472
[46] Matubayasi N and Nakahara M 1999 *J. Chem. Phys.* **110** 3291
[47] Huisman W J, Peters J F, Zwanenburg M J, de Vries S A, Derry T E, Abernathy D and van der Veen J F 1997 *Nature* **390** 379
[48] Choudhury N and Pettitt B M 2005 *J. Am. Chem. Soc.* **127** 3556
[49] Wu W, Zhang L, Liu S, Ren H, Zhou X and Li H 2016 *J. Am. Chem. Soc.* **138** 2815