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# *Structure of Ice Confined in Silica Nanopores*

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24     **Abstract**

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1    Observed anomalous thermodynamic properties of confined water such as deviations in the

2    melting point and freezing point motivate the determination of the structure of confined water as

3    a function of pore size and temperature. In this study, we investigate the dynamic evolution of

4    the structure of confined ice in SBA-15 materials with pore diameters of 4 nm, 6 nm, and 8 nm at

5    temperatures ranging from 183 K to 300 K using *in-operando* Wide-Angle X-Ray Scattering

6    (WAXS) measurements, X-Ray Partial Distribution Function (PDF) measurements, and classical

7    Molecular Dynamics (MD) simulations. Formation of hexagonal ice structures is noted in all the

8    three pore sizes. In silica nanopores with diameters of 4 nm, cubic ice formation is noted in

9    addition to hexagonal ice. Longer lasting hydrogen bonds and longer residence times of the

10   water molecules in the first coordination shell contribute to observed crystalline organization of

11   ice in confinement. Self-diffusion coefficients of confined liquid water predicted from classical

12   Molecular Dynamics (MD) simulations are four orders of magnitude higher compared to ice

13   formed in confinement. These experimental and simulation results provide comprehensive

14   insights underlying the organization of confined water and ice in silica nanopores and the

15   underlying physico-chemical interactions that contribute to the observed structures.

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17   **Keywords:** water; ice; silica; pores,  confinement; molecular dynamics, Wide Angle X-Ray

18   Scattering (WAXS) measurements

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22   **1.     Introduction**

1      Advancing predictive insights into ice hydrate formation can resolve several

2      technological challenges associated with achieving sustained fluid flow in subsurface

3      environments,[1-3] stability of hydrates in a changing climate,[4] and in harnessing gas hydrate

4      formation mechanisms to store or recover gases of interest.[5] While there is an extensive

5      understanding of the thermodynamics and phase transitions associated with bulk water and ice,

6      there is a limited fundamental understanding of the structure and organization of nano-confined

7      water and ice that contributes to anomalous thermodynamic behavior of nano-confined water

8      including the lower equilibrium melting point[6-8] and disordered hydrogen bonding networks of

9      nanoconfined water[9-11] compared to bulk water.

10      To probe the molecular scale basis of observed deviations in the phase transitions of

11      confined water, the development of innovative and robust hybrid experimental and molecular

12      simulation approaches is needed. Developing novel methods to understand the phase behavior of

13      confined fluids can pave the way to design fluids with specific thermophysical properties for

14      customized chemical, physical and biological applications. With this context, the liquid-solid

15      phase transitions of confined water have been studied using various experimental and theoretical

16      techniques such as vapor pressure measurements, dilatometry, differential scanning calorimetry

17      (DSC), nuclear magnetic resonance (NMR) spectroscopy, X-ray and neutron diffraction and

18      molecular simulations.[12-22] Silica nanopores have been used as confining environments to

19      investigate the phase transitions of confined water, since these materials provide well-defined

20      arrays of monodisperse cylindrical nanopores with tunable diameters ranging from 1 nm to 10

21      nm.[23, 24] Further, synthetic silica materials serve as an analog to siliceous matter that is abundant

22      in the natural and subsurface geologic environments.

1   Several advancements have been made towards our understanding of the thermodynamics

2 of confined water on freezing. The enhancement in the melting point depression of confined

3 water as the pore diameter decreases[6, 13, 25, 26] and the coexistence of liquid-solid phases in the

4 pore space at temperatures below the melting point of confined water[15] have been experimentally

5 established. The concept of premelted water at the surface walls and its influence on the melting

6 behavior of confined water was proposed.[15, 27, 28] Modifications to predictive relationships such

7 as the Gibbs-Thompson (GT) equation were developed based on these insights. According to the

8 modified GT equation, the melting point $T_m(R)$ of confined water decreases as a function of the

9 confinement space volume, $T_m(R) = T_m^{bulk} - \dfrac{K_{GT}}{R-d}$, where $T_m^{bulk}$ is 273.15 K, $K_{GT}$ is 53 ± 1 K nm,

10 $R$ is the confinement radius and $d$ is the premelted water layer between the confined ice and pore

11 wall which is about 0.4-0.7 nm.[7] Although the modified GT equation predicted the influence of

12 the extent of confinement on the melting point and suggested the liquid-solid coexistence, it does

13 not provide fundamental insights into several ambiguous aspects of the phase transition nature of

14 the confined water such as the effect of surface chemistry and the chemical potential on the

15 melting point profile.

16   In this context, the liquid-solid phase transition nature of confined water and the emerged

17 ice structures in carbon nanotubes with diameters ranging from sub-nanometers to about 2 nm

18 have shown profound deviations from bulk water such as the emergence of multiple ice

19 polymorphs and the depression/elevation in the melting/freezing temperatures.[29-32] For instance,

20 Takaiwa and co-workers[33] showed that confined water in nanotubes with diameters ranging from

21 0.9 nm to 1.7 nm form at least nine ice polymorphs at 0 K. Koga et al.[34] revealed that four ice

22 polymorphs are spontaneously emerged from liquid-like disordered phases confined in nanotubes

23 with a diameter of 1.4 nm at 200 K. Pugliese et al.[35] linked the freezing point of confined water

1  in carbon nanotubes to the nanotube diameter by investigating the state of water in nanotubes

2  with diameters ranging from 0.98 nm to 1.37 nm. The results indicated that freezing points of

3  confined water in nanotubes with diameter of 1.056 nm is 390 K. Agrawal and co-workers[36]

4  reported that the freezing transition of confined water in carbon nanotubes with diameters of

5  1.05-1.52 nm decreases as the pore diameter increases with the highest transition temperature of

6  105-115 $^{\circ}$C in the nanotube of 1.05 nm. Although these anomalies are well established in

7  synthetic carbon nanotubes, the phase transitions nature and ice structure of confined water in

8  earth-abundant porous silica materials are far less understood.

9  Despite previous experimental and computational studies are performed on the phase

10  transition of confined water in silica-based materials,[25, 27, 37-39] uncertainties in the structure and

11  dynamics of confined water still exist. The phase transition of confined water in silica pores with

12  a wide range of pore diameters and geometries has been found to obey a first-order transition,[7]

13  while other studies suggest that the transition occurs continuously.[40] Although several studies

14  have linked the melting point depression of confined water to the pore sizes and shapes,[41]

15  insights into the effect of the confining environment on the emergence of different ice

16  polymorphs are still lacking.

17  To address these uncertainties, we investigate the structure and organization of water

18  confined in silica nanopores using *in-situ* synchrotron Wide Angle X-Ray Scattering (WAXS)

19  measurements, X-Ray Pair Distribution Function (PDF) measurements, and classical molecular

20  dynamics (MD) simulations. Experiments and simulations are performed on confined water in

21  cylindrical SBA-15 silica pores with diameters of 4 nm, 6 nm, and 8 nm, and at temperatures in

22  the range of 183 K - 300 K to probe insights on the structure and dynamics of supercooled water

23  in confinement and the associated phase transitions in this temperature range. The hypothesis

that the differences in the hydrogen bonding of confined water molecules influence the structure of confined water is probed. Thus, this study aims to provide insights derived from experiments and simulations into the structure of ice as a function of confinement and temperature and the underlying hydrogen bonding behavior that contributes to the observed organization of confined water.

## 2.    Methods

### 2.1.    Experimental determination of the structural features of ice

The structures of ice formed in silica nanopores are determined using *in-situ* Wide Angle X-Ray Scattering (WAXS) measurements. Water is loaded in the powdered SBA-15 materials with pore diameters of 4 nm, 6 nm, and 8 nm (Sigma Aldrich). These SBA-15 materials comprise interconnected cylindrical pores with parallel alignment **(see Figure 1 (a))**. The silica materials are dried at 130 °C for 2 hours to remove the adsorbed water and impurities and then loaded with water. This drying protocol aimed to remove the physically adsorbed water on the SBA-15 surface rather than the chemically bound OH groups on the pores' surfaces. The SBA-15 materials loaded with water are filled in quartz capillaries with outer and inner diameters of 1.5 mm and 1.2 mm, respectively. The capillaries are loaded in the instrument and the samples are supercooled using liquid $N_2$ to 183 K using a cryostream cooler (Oxford cryo-stream 700). The samples are subsequently heated to room temperature (300 K) and measurements are taken during heating. To capture temperature-dependent changes in the confined water structure, the data are collected at 183 K, 200 K, 220 K, 240 K, 255 K, 273 K and 300 K. The samples are equilibrated for 10 minutes at each temperature before data acquisition. After the data acquisition, the samples are heated to the subsequent temperature.

1　　　　　WAXS measurements are performed at Beamline 6-ID-D in Sector 6 at Advanced Photon

2　　Source (APS) at Argonne National Laboratory (ANL).[42] The incident X-ray beam used has a

3　　wavelength of 0.206592 Å and an energy of 60 keV. During the measurements, the Varex

4　　CT4343 detectors are utilized to collect the scattered beam from the samples and the sample-to-

5　　detector distance for the WAXS measurements is 385.4 mm. The instrument calibrations are

6　　performed on a cerium dioxide ($CeO_2$) reference sample.[43, 44] The WAXS data are reduced using

7　　NIKA[45] algorithm embedded in Igor software (WaveMetrics) and the scattered intensity at each

8　　temperature is plotted as a function of the wavevector ($Q$) (where $Q = (4\pi/\lambda)\sin\theta$, $\lambda$ is the X-ray

9　　wavelength, and $\theta$ is half of the scattering angle). Background from the empty capillary at each

10　　temperature is also acquired and subtracted from the scattering intensities obtained from the

11　　samples in the capillary.

12　　　　　X-ray differential pair distribution functions ($D(r)$) are extracted and fitted from Small-

13　　Angle and Wide-Angle X-Ray Scattering (SAXS/WAXS) measurement using fit2D software.[46]

14　　The data are reduced, combined, and normalized to the form factor calculations of Wang and co-

15　　workers[47] as noted by Skinner and co-workers.[44] X-ray differential pair distribution function is

16　　calculated as follows, where $\rho$, $r$ and $g(r)$ are the density, radius, and the measured pair

17　　distribution function, respectively:

18　　$D(r) = 4\pi\rho r\left[g(r)-1\right]$　　　　　　　　　　　　　　　　　　　　　　(1)

19　　The obtained $D(r)$ contains the O-O and O-H interactions in the confined water molecules in 4

20　　nm, 6 nm and 8 nm sized pores.

21　　**2.2.　　Molecular dynamics (MD) simulations of the structure of ice**

1   The molecular scale mechanisms underlying the observed structure of ice are determined

2   using classical MD simulations. To obtain representative pore structures, cylindrical pores

3   terminated by -OH groups with diameters of 4 nm, 6 nm, and 8 nm are cleaved in silica surfaces

4   to obtain the material architectures representative of the X-ray scattering measurements **(Figure**

5   **1 (b))**. The -OH group density on the pore surface is about 8 nm$^{-2}$.[48, 49] The 4 nm, 6 nm and 8 nm

6   pores were filled with 592, 1571 and 2962 water molecules, respectively, to achieve a water

7   density of about 1 g/cm$^3$. The silica pores and water molecules are modeled using ClayFF[50] and

8   TIP5P[51] models **(see Table S1)** and the potentials account for the bonded and nonbonded

9   interactions. ClayFF accounts for the nonbonded interactions between the silica atoms and the

10  $O_{nonbridging}$-H bonds stretching only. TIP5P model is a five-site potential composed of Lennard

11  Jones (LJ) sites on the neutral oxygen, two positively charged hydrogens and two negatively

12  charged massless sites. The melting point of TIP5P model is 274 K at 1 bar which is consistent

13  with the experimental melting point of bulk water (273.15 K).[52] The TIP5P model has been used

14  extensively to model the behavior of water at low temperatures.[53-55]

15  The constructed initial configurations were optimized for geometry using the steepest

16  descent method for 50,000 steps. Simulated annealing algorithms are performed on the optimized

17  configurations under a constant number of particles, constant volume, and constant temperature

18  (NVT) ensemble for 120 ns. The system is equilibrated at 300 K, steeply quenched to 183 K

19  followed a systematic steep heating to 200 K, 220 K, 230 K, 235 K, 240 K, 245 K, 250 K, 255

20  K, 273 K and 300 K with 10 ns equilibrium time at each temperature point to be consistent with

21  the experimental WAXS measurements **(see Figure S1)**. The leapfrog integrator with a time step

22  of 1 fs is utilized to solve the equation of motion. Nose-Hoover thermostat is used to control the

23  simulation temperature.[56, 57] The short-range interactions are calculated within a cutoff of 1.2 nm,

1     while the long-range electrostatic interactions are treated using Particle Mesh Ewald (PME).[58]

2     During the MD simulation, bonding interactions accounted for bond stretching, angles bending

3     and dihedrals, while nonbonding interactions are calculated for van der Waals (vdW) and

4     electrostatic (ES) interactions. vdW and ES interactions are modeled using 12-6 LJ and

5     Coulomb's functions, respectively, as follows: $U_{ij} = \sum_{i<j} \left[ 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} \right]$ where

6     $\varepsilon_{ij}$ is the potential well depth, $\sigma_{ij}$ is the finite distance at which the interatomic distance is zero,

7     $r_{ij}$ is the distance between $i$ and $j$, $q_i$ and $q_j$ are the charges of $i$ and $j$, and $\varepsilon_o$ is the dielectric

8     permittivity of vacuum. LJ parameters (i.e., $\varepsilon_{ij}$ and $\sigma_{ij}$) for unlike molecular interactions are

9     calculated based on the Lorentz-Berthelot rule as follows: $\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ . MD

10     simulations are performed using GROMACS 2018 software.[59]

11     **3.**       **Results and Discussions**

12     **3.1.**      **The temperature-dependent structure of confined water**

13         The hypothesis that the structure of ice in confinement varies with pore diameter is

14     probed experimentally using *in-situ* WAXS measurements. The *in-situ* WAXS intensity curves

15     of water confined in 4 nm, 6 nm and 8 nm sized silica pores as a function of the $Q$ at

16     temperatures ranging from 183 K to 300 K are shown in **Figure 2**. The main peaks in the

17     intensity curves, at $Q$ in the range of of 2 Å$^{-1}$ to 3 Å$^{-1}$ for 4 nm, 6 nm and 8 nm pores,

18     respectively, are fitted using Lorentzian function to probe the full width half maximum (fwhm)

19     to quantitatively analyze the changes in the intensity of the peaks as a function of temperature

20     **(see Figure S2)**.

1        The WAXS profiles demonstrate a clear dependence of the structure of ice on pore

2    diameters of 4 nm, 6 nm, and 8 nm and tempertures ranging from 183 K to 255 K. Significant

3    shifts in the peak positions are not detected, though new peaks arise as the temperatures change

4    from 183 K to 273 K. These data show that stable ice structures are formed at temperatures

5    below the melting point of the confined ice, which is consistent with the findings of Morishige

6    and co-workers.[60] Ice structures are a function of the pore size. Cubic ice and hexagonal ice are

7    formed in silica nanopores with pore diameters of 4 nm. The formation of mixture of hexagonal

8    and cubic ice in 4 nm pores is consistent with the findings of Thangswamy and co-workers[61] who

9    studied the evolution of ice structue in 2.5 nm cylinderical silica pores. Thangswamy et al.

10   attributed the formation of mixture of hexagonal and cubic ice to the nucleation of ice crystals

11   inside the pore at low temperatures (below 240 K) that creep out of the pores to form bulk

12   crystals with hexagonal and cubic polymorphs. In contrast, hexagonal ice is formed in pores with

13   diameters of 6 nm and 8 nm. These observed structures of ice in confinement are consistent with

14   previous studies.[62, 63] The intensity of the peaks representing crystalline ice is significantly

15   reduced after 255 K and these peaks disappear at 300 K in all the pore sizes, suggesting the total

16   melting of the formed ice.

17        The temperature-dependent structural alterations of the confined water are also evident

18   from the profiles of the experimentally obtained X-Ray Differential Pair Distribution Functions

19   (PDF) represented by $D(r)$ **(see Figure 3)** and radial distribution functions determined from

20   molecular dynamics (MD) simulations represented by $g(r)$ **(see Figure 4 (a-c))**. Water confined

21   in 4 nm sized pore formed single crystals of ice, thus a reliable differential pair distribution

22   functions could not be extracted. The temperature-dependent $D(r)$ profiles show well defined

23   peaks for the first and second shells at about 2.8 Å and 4.6 Å, respectively. As the temperature

1    increases, the first peak shifts to longer distances and the second shell decreases in intensity as

2    the confined water adopts a more tetrahedral structure.[64] At 300 K, $D(r)$ shows similar local

3    structural arrangements of confined water in all the pores with broadening of the first peak

4    between 8 nm and 6 nm **(see Figure S3)**.

5           The respective positions of the first and second coordination shells corresponding to the

6    organization of water are calculated to be $2.78 \pm 0.03$ Å and $4.52 \pm 0.02$ Å, respectively, in 4 nm,

7    6 nm and 8 nm sized pores **(see Figure 4 (a-c)).** These positions are obtained from the radial

8    distribution profiles, $g(r)$ using molecular dynamics simulations **(see Figure 4 (a-c)).** The

9    systematic arrangement of water molecules with decreasing temperature is evident from the

10   increasing intensity of the peak that corresponds to the first coordination shell. The rate of

11   increase in the peak that corresponds to the first coordination shell is $0.000259 \pm 0.000014$ Å K$^{-}$

12   $^{1}$, $0.000482 \pm 0.000021$ Å K$^{-1}$ and $0.000314 \pm 0.000018$ Å K$^{-1}$ in 4 nm, 6 nm, and 8 nm sized

13   pores, respectively. The peak positions that correspond to the first and second coordination shells

14   and the rates of change with temperature agree with prior experimental and simulation results

15   after accounting for confinement effects.[64-68] These studies are summarized in **Table 1**.

16          The transition of ordered polymorphs of ice at low temperatures to amorphous structures

17   and a decrease in the number of molecules in the first hydration shell of water with increasing

18   temperature is evident from the reduction of $g(r)$ peak height (**Figure 4**). Changes in the

19   structure and density of interfacial water are evident from the $g(r)$ representing the O-O

20   coordination of water at the silica surface **(see Figure S4)**.

21          The oxygen-oxygen coordination number ($n_{oo}(r)$) **(Figure 4 (d-f))** was also calculated to

22   determine the number of atoms with the distance $r$ by integrating $g(r)$ as follows:

1  $$n_{OO}(r) = 4\pi\rho \int_0^r r^2 g(r) dr \qquad\qquad\qquad\qquad (2)$$

2  In the expression above, $\rho$ is the number density of confined water (determined as the total

3  number of molecules divided by the pore volume). The profiles of $n_{OO}$ indicates the existence of

4  isosbestic point in the applied range of temperatures. Isosbestic point is defined as the point at

5  which the probability of finding an oxygen atom surrounding another oxygen atom is constant

6  with temperature.[66, 67] The position of the isosbestic point for confined water is comparable to

7  that of bulk water, which is consistent with previous studies.[64, 67] However, the corresponding

8  $n_{OO}$ of confined water is lower than that of bulk water over the same range of temperatures. The

9  oxygen-oxygen coordination number, $n_{oo}$ (r)  is 4.39 ± 0.15 and 4.3 ± 0.3 at the range 234-366 K

10  as suggested by Pathak and co-workers[67] and Skinner and co-workers,[66] respectively. The

11  observation of the isosbestic point implies that the first coordination shell of confined water

12  shifts slightly from 2.72 Å (the position of the first peak) to 3.25 Å (the position of the isosbestic

13  point) as the temperature changes from 183 K to 300 K. In other words, the number of molecules

14  in the first shell remains constant within the isosbestic point radius and does not exchange with

15  the outer shells which consequently implies that the hydrogen bonding rearrangement occurs

16  separately within each shell defined as below or above 3.25 Å.[67] Further, the transition in the

17  structure of confined water at 255 K is also evident from the coordination number profiles as the

18  flattening in the $n_{oo}$ curves in the radius between 2.8 Å and 3.4 Å decreases substantially and the

19  curves become more linear with the radius after 255 K **(see Figure 4 (d-f))**.

20          The tetrahedral structure of ice and the absence of interstitial water molecule and

21  additional neighbor molecules in the first coordination shell of water molecules[69] is evident from

22  the plateau around a coordination number of 3.7 at low temperatures of 183-255 K. The

1    existence of interstitial water molecules at 273 K and 300 K is evident from the absence of this

2    plateau, which is consistent with structure of amorphous water.[43, 70] The formation of structured

3    ice at low temperatures is also observed from the MD simulations **(see Figure 5 and Figure 6).**

4    **Figure 5** shows snapshots of the front and side views of the hexagonal and cubic structures of

5    ice that extend along the pore length (z-direction). At low temperatures of 183 K and 200 K, the

6    hexagonal ice structures are abundant in the 4 nm, 6 nm and 8 nm pores.

7          The fraction of hexagonal ice formed in confinement  decreases slightly as the

8    temperature increases to 255 K and totally dissapears at 300 K, as indicated by the 2D density

9    maps of the confined water molecules in 4 nm, 6 nm and 8 nm pores that obtained from MD

10   simulations **(see Figure 6)**. The low-density and high-density regions that stem from the

11   formation of structured water are evident at 200 K in all the pores. The contrast between the low-

12   density and high-density regions start to decrease at 250 K due to the breaking of the formed

13   structures at lower temperatures and the emergence of amorphous structures. On heating the

14   systems to 300 K, all the formed structures at 200 K disappear and the only observed contrast in

15   the pore is between the interfacial water and free confined water. At 300 K, the interfacial water

16   showed higher densities due to the favorable interaction with the hydrophilic silica surface which

17   is consistent with previous MD simulation studies.[71-73] It is interesting to observe that the

18   contrast between the interfacial water and free water decrease significantly at low temperatures,

19   suggesting that the surface effect on the confined water increases with temperature.

20   **3.2.    The nature of the phase transition of confined water**

21          In addition to the structural characteristics of the confined water, the hydrogen bonding

22   nature between the water molecules, both the free water and the interfacial water at the pore

23   surface, provide critical insights into the nature of the phase transition and the local structure of

the water molecules in the temperature range of interest which is 183 K – 300 K. Our

calculations from molecular dynamics simulations showed that the the number of hydrogen

bonds per confined water molecule increases steeply from slightly less than 2 to about 3.3 as the

temperature decreased from 300 K to 183 K **(see Figure 7 (a))**. The steep change in the

hydrogen bonds as the system is quenched suggests a first-order transition of confined water in 4

nm, 6 nm, and 8 nm pore sizes which is consistent with previous studies.[11, 55, 74] The number of

hydrogen bonds per water molecule at temperatures between 183 K and 230 K is greater than 3,

indicating the formation of 3D water networks in confinement. The number of hydrogen bonds

per confined water molecule decreases continuously from about 3.3 to about 2.7 as the

temperature increases from 183 K to 255 K. First-order transitions are also noted on heating the

confined water from 255 K to 273 K and from 273 K to 300 K where the number of hydrogen

bonds decreased to about 2.3 and to about 1.9, respectively. These two first-order transitions are

also evident from the WAXS intensities and the *D(r)* profiles with an increase in the temperature

**(see Figure 2 and Figure 3).**

The formed hydrogen bonds between free water molecules exhibit a lifetime of about 2

ns at low temperatures of 183 K **(see Figure S5)**. The average lifetime of the water-water

hydrogen bonds decreased slightly as the system was heated to about 240 K, followed by a

dramatic decrease to reach about 0.003 ns at 273 K and 300 K. The long-lasting hydrogen bonds

at low temperatures indicate the formation of stable clusters in the confined water outside the

interfacial water layer.

Interfacial hydrogen bonding with the hydroxyl groups on the pore surface reduce the

number of hydrogen bonds formed between the free water molecules. The number of hydrogen

bonds between the interfacial water layer and the OH groups on the pore surface increases with

1  the pore diameter due to the increase in the number of the OH groups on the surface **(see Figure**

2  **7 (b))**. Interestingly, the phase transitions of confined free water molecules differ from that of

3  water molecules bonded to the pore surfaces. The hydrogen bonding of interfacial water showed

4  temperature-independent profiles in 4 nm, 6 nm and 8 nm sized pores. The observed first-order

5  phase transitions of confined free water are not evident from the hydrogen bonding profiles of

6  interfacial water. The water-pore hydrogen bonds profiles indicate that the interfacial water layer

7  retain premelted water properties even at temperatures as low as 183 K which agrees with

8  previous studies.[7, 8]

9  The stability of the formed water structures as the temperature changes and time taken

10  by water molecules to remain in contact with each other at each temperature are probed by

11  calculating the residence autocorrelation function $(C_R(t))$ **(see Figure 8).** The contact period of

12  the water molecules was monitored by computing $C_R(t)$ as follows[75, 76]:

13  $$C_R(t) = \frac{\langle O_w(t)O_w(0)\rangle}{\langle O_w(0)O_w(0)\rangle}$$  (3)

14  In the expression above, $O_w(t)$ describes whether the molecule is in the first coordination shell

15  of the water molecule at a time $t$, $O_w(t)$ is equal to one if the molecule exists in the first

16  coordination shell at time $t$, otherwise it equal to zero. The residence autocorrelation function is

17  calculated from the center of the mass of the water molecules. Faster decay of $C_R(t)$ from 1 to 0

18  is an indicative of the shorter contact between the water molecules. Longer decay time is evident

19  at low temperatures and the decay time systematically decreases with an increase in temperature.

20  A decay time of about 3.6 ns was noted at temperatures up to 240 K. A substantial decrease in

21  the decay time to less than 0.1 ns was noted at 300 K. The longer decay time at low temperatures

22  suggests that the water molecules in the first coordination shell exchange more slowly with those

from outside the first shell. The longer contact time of the water molecules facilitates the rearrangement of the water molecules within the first coordination shell to form hydrogen bonding networks that result in ice with crystalline structures. The trend in the contacting time between the water molecules represented by $C_R(t)$ is consistent with the lifetime of hydrogen bonds between the confined water molecules.

Similarities in the transitions associated with water-water hydrogen bonding profiles and the potential energy of the confined water molecules are noted (see **Figures 7 (a) and 9 (a)**). Potential energy represents the summation of bonded and nonbonded interactions of water molecules, inculding bond stretchings, angle bendings, diherdrals, van der Waals and electrostatic interactions. The potential energy of the confined free water molecules decreased steeply by about 8 kJ/mol on quenching the systems from 300 K to 183 K which confirms the first-order transition noted from the hydrogen bonding profiles **(Figure 7 (a))**. This drop in potential energy is in agreement with the data corresponding to the freezing transition of bulk water of 7 kJ/mol[77] and differs from that of confined water (5.6 kJ/mol)[11] predicted using TIP4P models. This first-order phase transition is followed by a continuous increase in the potential energy on heating the system from 183 K to 255 K, followed by two steep increases on heating from 255 K to 273 K and from 273 K to 300 K, which implies two other first-order phase transitions. The increase in the potential energy on heating the system from 255 K to 273 K and from 273 K to 300 K is about 3 kJ/mol, which is comparable to that of the transition of confined TIP5P nanofilms[55] and to the melting of bilayer ice.[78]

Potential energy of the interfacial water molecules on the pore surface are dependent on the size of the pore. Larger pores have more number of water molecules bound to the pore surface which contribute to higher potential energy (the absolute value of the potential energy)

1   **(see Figure 9 (b))**. The negative sign of the potential energy indicates the attractive nature of

2   water-pore interactions. The potential energy profiles of interfacial water molecules (**Figure 9**

3   **(b)**) are less sensitive to changes in temperature compared the confined water molecules (**Figure**

4   **9 (a)**). The hydrogen bonding and potential energy profiles show that the first-order phase

5   transitions of the interfacial water molecules differ from that of confined water.

6

7   **3.3.    The temperature-dependent dynamics of confined water**

8   To probe the changes in the dynamics of water confined in silica nanopores during

9   freezing, the diffusivities of confined water as a function of temperature are probed **(see Figure**

10  **10)**. Prior studies demonstrated significant differences in the diffusivities of ice formed in

11  unconfined environments and in bulk water. For example, the diffusion coefficient of bulk ice is

12  $\sim 10^{-9}$ cm$^2$/sec, while that of bulk liquid water is $\sim 10^{-5}$ cm$^2$/sec.[74, 79-81] However, few studies

13  have linked the phase transitions of confined water and structures of ice to the corresponding

14  diffusive transport behavior. The diffusivities of the confined water and ice differ by nearly four

15  orders of magnitude.

16  This orders of magnitude change in the diffusion coefficient at temperatures in the range of 183

17  K to 300 K is comparable to that of the liquid to crystalline ice transition obtained both

18  experimentally and computationally.[11, 82] The diffusivity changes by less than one order of

19  magnitude between 183 K and 220 K followed by an increase of three orders of magnitude on

20  heating to 255 K. At 273 K and 300 K, the diffusivity plateaus at about $10^{-5}$ cm$^2$/sec which is

21  consistent with that of bulk water.

22  The self-diffusion coefficients of confined water are dependent on the pore size with

23  larger pore sizes of 8 nm sizes having higher diffusivities compared to 6 nm and 4 nm pores.

These observations are consistent with observations that narrower pores contribute to lower diffusivities of confined water at various surface chemistries.[71, 83-85] Further, the mean square displacement (MSD) profiles **(see Figure S6)** indicate a transition from a ballistic motion ($MSD \ \alpha \ t^2$), where $t$ is the time, to a diffusive motion ($MSD \ \alpha \ t$) at high temperatures, which is a characteristic of typical liquid behavior.[55] At temperatures below the melting points, the *MSD* profiles are less dependent on the time with time independent diffusivities noted at 183 K and 200 K in all the pore sizes, suggesting that all the confined water had turned to ice. The change in the MSD profiles of confined water in 4 nm, 6 nm and 8 nm pores confirm the melting of the formed ice inside the silica pores at higher temperatures which is in agreement with the experimental diffraction measurements observed inside cylindrical silica nanopores.[63]

## 4.    Conclusions

Several important insights into the structure, organization, and nano-scale diffusivity of confined water and ice in cylindrical silica pores with sizes of 4 nm, 6 nm, and 8 nm at temperatures ranging from 183 K to 300 K are obtained using *in-situ* Wide-Angle X-Ray Scattering (WAXS) measurements, X-Ray Pair Distribution Function (PDF) measurements and classical molecular dynamics (MD) simulations. Hexagonal ice structures are dominant in silica nanopores with diameters of 4 nm, 6 nm, and 8 nm. Cubic ice is noted in addition to hexagonal ice in silica nanopores with a diameter of 4 nm. The formation of hexagonal crystalline ice is confirmed using MD simulations. The profiles of hydrogen bonding and the potential energy obtained from the MD simulations indicate the existence of multiphase transitions as the system is quenched from 300 K to 183 K, heated from 255 K to 273 K, and from 273 K to 300 K. The structure of the formed ice is characterized by longer lasting hydrogen bonds, the presence of isosbestic point and longer contacting time with the molecules in the first coordination shell

compared to liquid water. These insights inform emerging efforts to tune the structure and organization of hydrates for energy and environmental applications. The applied experimental-computational method in this study can be extended to probe the properties of confined fluids in a wide range of porous materials and to achieve a predicitive controlling over the properties of these fluids.

**Associated Content**

The supporing information file contains detailed description on the methods and supplementary data supporting the finding of the paper including Wide Angle X-Ray Scattering (WAXS), X-Ray Pair Distribution Function (PDF), hydrogen bonding lifetime, radial distribution functions (RDFs), and the mean square displacement of water.

**Acknowledgment**

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18   **Table 1.** Comparison of 'r' values for first and second coordination shells of O-O bonds for
19   confined ice strutures between 200-250 K, and 273 K with those reported in the literature

20

| First shell (r (Å)) | Second shell (r (Å)) | Measurement approach | Confinement | Type of Ice | Ref. |
|---|---|---|---|---|---|

| T = 200 - 250 K | | | | | |
|---|---|---|---|---|---|
| 2.8 | 4.6 | Experimental | SBA-15 (pore = 6 nm, 8 nm) | Crystalline | This work |
| 2.78 ± 0.03 | 4.52 ± 0.02 | MD simulations | Silica (pore = 4 nm, 6nm, 8 nm) | Crystalline | This work |
| 2.9 | 4.5 | Experimental | Vycor glass (pore = 4 nm) | Crystalline | Ref. 86 |
| 2.78 | 4.26 | Experimental | MCM-41 (pore = 2.8 nm) | | Ref. 87 |
| 2.36 | 4.6 | Experimental | MCM-41 (pore = 2.83 nm) | Non-crystalline | Ref. 88 |
| 2.8 | 4.1 | Experimental @ 77K | Silica gel (pore = 6 nm) 20% hydrated | Crystalline | Ref. 89 |
| T = 273 K | | | | | |
| 2.8 | 4.6 | Experimental | SBA-15 (pore = 6 nm, 8 nm) | | This work |
| 2.78 ± 0.03 | 4.52 ± 0.02 | MD simulations | Silica (pore = 4 nm, 6nm, 8 nm) | | This work |
| 2.9 | 4.5 | Experimental | Vycor glass (pore = 4 nm) | | Ref. 86 |
| 2.76 | 4.15 | Experimental | MCM-41 (pore = 2.8 nm) | | Ref. 87 |
| 2.36 | 4.6 | Experimental | MCM-41 (pore = 2.83 nm) @ 268K | | Ref. 88 |

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8 **Captions for figures**

9 **Figure 1.** (a) Schematic representation of the experimental setup for Wide-Angle X-Ray
10 Scattering (WAXS) measurements and (b) the snapshot represents the geometry of the
11 cylindrical silica pore with a diameter of 4 nm and confined water molecules. Silica and water

1    atoms are shown by the VDW and CPK drawing methods, respectively, implemented in VMD
2    visualization software.

3    **Figure 2.** Identification of the crystalline features of ice in Wide-Angle X-ray Scattering
4    (WAXS) patterns. Crystalline ice is observed in silica (SBA-15) nanopores with pore diameters
5    of 4 nm, 6 nm, and 8 nm at temperatures ranging from 183 K to 273 K. (*) indicates dominant
6    cubic ice phase with minor hexagonal ice contribution.

7    **Figure 3.** X-ray differential pair distribution functions of O-O and O-H interactions of confined
8    water in 6 nm and 8 nm sized pores as a function of temperature.

9    **Figure 4.** The radial distribution function of oxygen-oxygen atoms in water molecules in 4 nm
10   **(a)**, 6 nm **(b)** and 8 nm **(c)** silica pores. The corresponding coordination number of oxygen-
11   oxygen in 4 nm **(d)**, 6 nm **(e)** and 8 nm **(f)** silica pores as a function of the temperature are
12   obtained from molecular dynamics simulations to determine the isosbestic point of water in
13   confinement.

14   **Figure 5.** Snapshots representing the front and side views of the formed hexagonal ice structures
15   in silica nanopores with diameters of 4 nm **(a and b)** and 8 nm **(c and d)** and cubic ice in 4 nm **(e**
16   **and f)** obtained from the molecular dynamics simulations. The snapshots were taken at a
17   temperature of 200 K. Structured water molecules are shown using VDW representation and
18   implemented in the VMD visualization software.

19   **Figure 6.** The density maps of the confined water molecules show the progressive melting of the
20   confined ice as the temperature increase in 4 nm, 6 nm and 8 nm silica pores. The density maps
21   are averaged over the entire 10 ns of the temperature of interest.

22   **Figure 7.** The number of water-water hydrogen bonds normalized by the number of the
23   simulated water molecules as a function of temperature and simulation time are shown in **(a)**.
24   The total number of hydrogen bonds between the interfacial water molecules and the hydroxyl
25   groups in the pore surface as a function of temperature and the simulation time are shown in **(b)**.

26   **Figure 8.** The residence autocorrelation function of water molecules in 4 nm (a), 6 nm (b) and 8
27   nm (c) silica pores as a function of the contact time. The residence autocorrelation function is
28   averaged over the entire 10 ns of the simulation time at each temperature.

29   **Figure 9.** Potential energy associated with the interactions of the water molecules normalized by
30   the total number of water molecules in 4 nm, 6 nm and 8 nm silica pores are shown **(a)**. The
31   steep changes in the potential energy profiles are shaded to emphasize the regions where the
32   first-order transitions occur. The interaction energy of interfacial water molecules with the
33   surface of 4 nm, 6 nm and 8 nm silica pores are shown **(b)**.

34   **Figure 10.** The self-diffusion coefficients of confined water along the pore length ($D_Z$) as a
35   function of the temperature and the pore diameter predicted from molecular dynamics
36   simulations are shown. The error bars represent the standard deviations based on simulations
37   performed in triplicate.

**Figure 1.** (a) Schematic representation of the experimental setup for Wide-Angle X-Ray Scattering (WAXS) measurements and (b) the snapshot represents the geometry of the cylindrical silica pore with a diameter of 4 nm and confined water molecules. Silica and water atoms are shown by the VDW and CPK drawing methods, respectively, implemented in VMD visualization software.

**Figure 2.** Identification of the crystalline features of ice in Wide-Angle X-ray Scattering (WAXS) patterns. Crystalline ice is observed in silica (SBA-15) nanopores with pore diameters of 4 nm, 6 nm, and 8 nm at temperatures ranging from 183 K to 273 K. (*) indicates dominant cubic ice phase with minor hexagonal ice contribution.

**Figure 3.** X-ray differential pair distribution functions of O-O and O-H interactions of confined water in 6 nm and 8 nm sized pores as a function of temperature.

Figure 4. The radial distribution function of oxygen-oxygen atoms in water molecules in 4 nm **(a)**, 6 nm **(b)** and 8 nm **(c)** silica pores. The corresponding coordination number of oxygen-oxygen in 4 nm **(d)**, 6 nm **(e)** and 8 nm **(f)** silica pores as a function of the temperature are obtained from molecular dynamics simulations to determine the isosbestic point of water in confinement.

**Figure 5.** Snapshots representing the front and side views of the formed hexagonal ice structures in silica nanopores with diameters of 4 nm **(a and b)** and 8 nm **(c and d)** and cubic ice in 4 nm **(e and f)** obtained from the molecular dynamics simulations. The snapshots were taken at a temperature of 200 K. Structured water molecules are shown using VDW representation and implemented in the VMD visualization software.

**Figure 6.** The density maps of the confined water molecules show the progressive melting of the confined ice as the temperature increase in 4 nm, 6 nm and 8 nm silica pores. The density maps are averaged over the entire 10 ns of the temperature of interest.

**Figure 7.** The number of water-water hydrogen bonds normalized by the number of the simulated water molecules as a function of temperature and simulation time are shown in **(a)**. The total number of hydrogen bonds between the interfacial water molecules and the hydroxyl groups in the pore surface as a function of temperature and the simulation time are shown in **(b)**.

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2  **Figure 8.** The residence autocorrelation function of water molecules in 4 nm (a), 6 nm (b) and 8
3  nm (c) silica pores as a function of the contact time. The residence autocorrelation function is
4  averaged over the entire 10 ns of the simulation time at each temperature.

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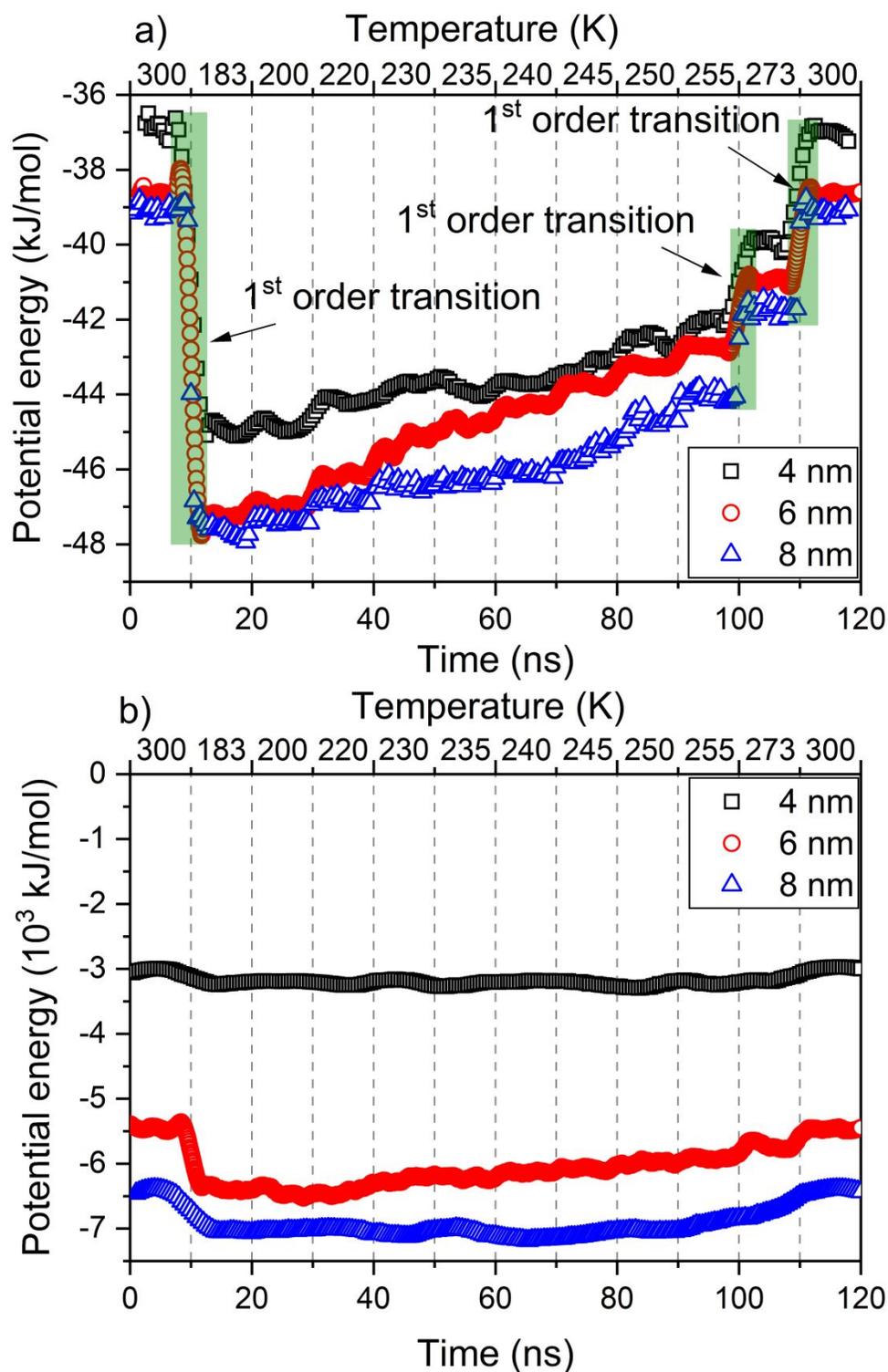
Figure 9. Potential energy associated with the interactions of the water molecules normalized by the total number of water molecules in 4 nm, 6 nm and 8 nm silica pores are shown (a). The steep changes in the potential energy profiles are shaded to emphasize the regions where the first-order transitions occur. The interaction energy of interfacial water molecules with the surface of 4 nm, 6 nm and 8 nm silica pores are shown (b).

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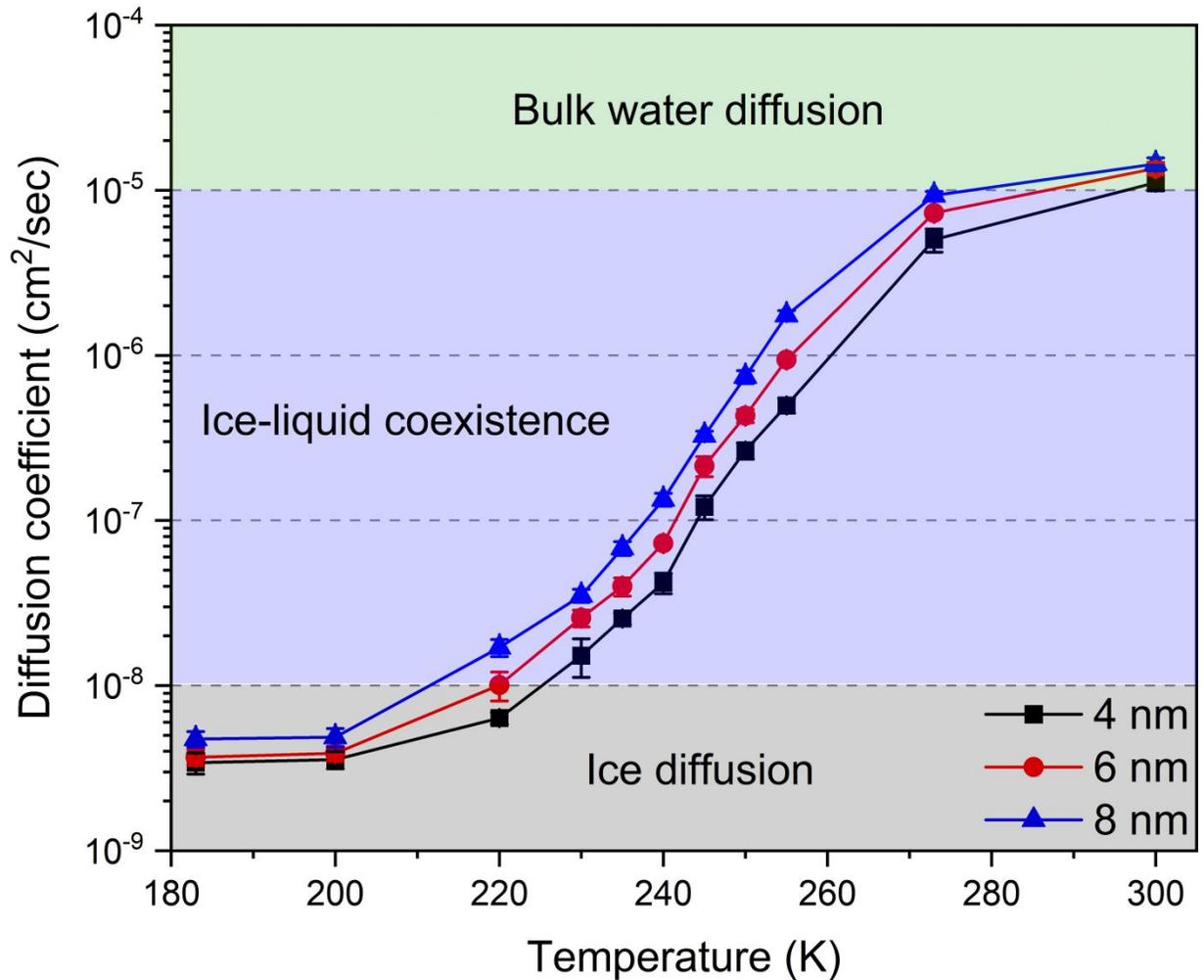


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**Figure 10.** The self-diffusion coefficients of confined water along the pore length ($D_Z$) as a function of the temperature and the pore diameter predicted from molecular dynamics simulations are shown. The error bars represent the standard deviations based on simulations performed in triplicate.

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