KIM REVIEW
https://kimreview.org/

Volume 4, Article 03, 2026
DOI:10.25950/6e3f95ad

Ice in a tube: new phases of water at the nanoscale and a solid–liquid critical point

Commentary by

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on

Formation of ordered ice nanotubes inside carbon nanotubes
K. Koga, G. T. Gao, H. Tanaka, and X. C. Zeng, Nature, 412:802–805 (2001).

Received April 9, 2026
Published May 29, 2026

Statement of Significance

The 2001 paper by Koga, Gao, Tanaka, and Zeng [1] is a landmark in the molecular simulation of confined fluids. Using molecular dynamics simulations, they revealed that water encapsulated inside single-walled carbon nanotubes of sub-nanometer diameter can form entirely new phases of ice - square, pentagonal, hexagonal, and heptagonal nanotube structures - with no counterpart in bulk water. More remarkably, the paper presented evidence for a solid-liquid critical point in a quasi-one-dimensional system, a phenomenon thermodynamically forbidden in the bulk. Published in *Nature* at a time when carbon nanotubes were attracting intense interest as nanoscale capillaries and templates, this paper launched a new field of research. It has accumulated over a thousand citations and continues to motivate work on nanofluidics, nanotube-confined phase behavior, pressure in nanoscale systems, and the use of molecular simulation to uncover fundamentally new physics inaccessible to experiment alone.

A new kind of ice

Water has long been known to be an unusually complex substance. At the time of the Koga et al. paper [1], thirteen crystalline polymorphs of ice had been identified experimentally. This diversity reflects the remarkable flexibility of the hydrogen-bond network: the ability of water to donate two hydrogen bonds and accept two more give it the ability to arrange in a variety of network topologies, with a preference for tetrahedrally-coordinated networks at low to moderate pressures. Could the geometry of the local environment override these tendencies and produce something qualitatively different?

The setup of Koga et al. was simple: water molecules, described by the TIP4P force field, confined inside armchair single-walled carbon nanotubes (SWCNs) spanning roughly 1.1 to 1.4 nm in diameter, with chiral vectors ranging from (14,14) to (18,18). The nanotube-water interaction was modeled as a smooth, structureless Lennard-Jones cylinder, integrated analytically over the nanotube surface. This choice, while approximate, ensures that any emerging order arises from the water-water interactions under cylindrical confinement, not from commensurability with the nanotube lattice. Molecular dynamics simulations at constant temperature and axial pressure were carried out on isobaric and isothermal paths in the T-P_{zz} phase diagram, running for 10-200 ns - one to two orders of magnitude longer than typical water simulations of the period to obtain well-equilibrated structures.

What emerged was striking. In the wider nanotubes, cooling at 50 MPa produced a sharp, discontinuous drop in potential energy accompanied by a hysteresis loop on re-heating: a classic signature of a first-order phase transition. Structural analysis revealed the low-temperature phase to be a hollow, quasi-one-dimensional (quasi-1D) nanotube composed of stacked hexagonal ($n = 6$) or heptagonal ($n = 7$) water rings, respectively. Every water molecule in these rings satisfies the bulk ice rule: four hydrogen bonds, double donor, double acceptor. The resulting structure has the hollow-tube motif that is a natural consequence of confining the hydrogen-bond network in a cylindrical shell: molecules move to the periphery and there is no molecule at the axis.

In the narrower tubes, a qualitatively different scenario played out. The potential energy dropped smoothly on cooling, with no hysteresis - a continuous transformation from liquid-like to solid-like. The low-temperature phases were square ($n = 4$) and pentagonal ($n = 5$) nanotube structures. In these narrower pores the liquid phase itself adopts a hollow-tube structure with rudimentary square or pentagonal order, so that there is no abrupt symmetry change to mark a first-order transition. The continuity of the transformation was confirmed by the diffusion coefficient, which dropped smoothly from liquid-like values (~10^{-5} cm^2/s) to essentially zero without a sharp threshold.

The phase behavior becomes more complex at higher axial pressures. At 200 MPa in the smallest (14,14) tube, water undergoes a first-order transition directly to the pentagonal nanotube, bypassing the square structure. At 500 MPa, it transforms continuously into the pentagonal phase. The coexistence of continuous and discontinuous transitions between phases of different symmetry in a single pore diameter as a function of pressure is itself unusual, and the phase diagram constructed by Koga et al. has no bulk analogue.

A critical point between solid and liquid

The most surprising prediction in [1] is the existence of a solid-liquid critical point. In three-dimensional systems, first-order melting transitions are governed by symmetry: the solid and liquid phases are always distinguishable by the presence or absence of long-range positional order, so the first-order boundary between them extends without limit (or until it meets another phase boundary) on the phase diagram. A critical point for a solid-liquid transition is forbidden in 3D because the symmetry difference between the two phases cannot be continuously tuned away.

In one-dimensional (or quasi-1D) systems, this argument breaks down. Ising showed in 1925 that a strictly 1D system with short-range interactions cannot undergo a phase transition at any finite temperature [2]; the corollary is that the 1D “critical point” is at T = 0 K. Koga et al. proposed something more nuanced: that in the narrow (14,14)

SWCN, the square nanotube phase and the pentagonal nanotube phase (one liquid-like and one solid-like) can be connected by a path that circumvents the first-order boundary if that boundary terminates at a critical point at finite temperature and pressure.

The evidence presented in [1] is compelling. On the 280 K isotherm, the system shows a hysteresis loop between ~170 and ~200 MPa in both the potential energy and the volume - a first-order transition. On the 300 K isotherm, the transformation is continuous. On the 330 and 360 K isotherms, the changes become progressively smoother. The isothermal data bracket the critical point between 280 and 300 K. The first-order boundary on the T-P_{zz} diagram, confirmed by free-energy calculations, terminates at this critical point. Below it, one can distinguish a square liquid from a pentagonal solid; above it, the distinction disappears.

This prediction was intriguing. The idea that a phase boundary between states of different symmetry could end at a critical point was thought to be forbidden. The quasi-one-dimensionality of the confined system lifts this restriction, and Koga et al. provided the first simulation evidence that such a transition is physically realizable.

Simulation methodology and its context

The methods chosen by Koga et al. deserve attention. The TIP4P water model was already well-established for bulk simulations, having been parameterized to reproduce bulk liquid properties. Its use for a confined system at pressures up to 500 MPa was a reasonable extrapolation; subsequent work revisited this choice with more modern force fields, but the qualitative picture (square, pentagonal, hexagonal, and heptagonal ice nanotubes, continuous vs. first-order transitions) remained [3], [4]. The constant-T, constant-P_{zz} ensemble was appropriate because the nanotube axis is the mechanically relevant direction: water can flow in and out along this axis under a real applied pressure. The use of a smooth, structureless nanotube potential reduced computational cost and avoided spurious commensurability effects, allowing the authors to study a wider range of tube diameters and pressures than would otherwise have been feasible in 2001.

The simulation times (up to 200 ns for selected state points) were exceptional for that era. The importance of long simulations for nucleation and phase-transformation kinetics is well known, as nucleation is a rare event and short runs often get trapped in metastable states. Koga et al. were scrupulous in verifying equilibration by checking for reproducibility on both cooling and heating branches, and they identified genuine hysteresis (implying first-order transitions) rather than artifacts of insufficient equilibration. This level of care was not universal in the field and contributed to the confidence with which the community received the results.

The free-energy calculations used to locate the phase boundaries (both the chemical potential for the hexagonal ice nanotube and the grand-potential densities for the square and pentagonal phases) followed methods that were established but nontrivial to implement. The agreement between the free-energy results and the phase boundaries inferred from the MD hysteresis loops provided a strong internal check on the conclusions.

A broader context: in 2001, the molecular simulation of carbon nanotube systems was still in its early stages, and few groups had the computational resources or methodological expertise to carry out simulations of this quality. The paper appeared the same year as experimental demonstrations of water filling and single-file transport in nanotubes [5], and it set the theoretical framework within which those experiments would be interpreted.

Impact on the field

The paper has attracted more than a thousand citations over two decades, with no sign of diminishing interest. A survey of the citing literature reveals the breadth of impact across molecular simulation, condensed matter physics, materials science, and chemical engineering.

The most direct line of work has been theoretical and computational extensions of the phase diagram. Subsequent simulations examined the effect of force field choice: it is now established that the precise temperatures and pressures at which the new ice phases appear depend sensitively on the water model used [4], [6], [7], but the topological features of the phase diagram (square, pentagonal, hexagonal ice nanotubes; continuous vs. first-order transitions; the solid–liquid critical point) have been confirmed with TIP3P, TIP5P, SPC/E, and more recent machine-learned potentials [4], [8], [9]. The critical point itself has been examined through finite-size scaling and direct free-energy methods, and the evidence for its existence has strengthened [3], [9].

A second major thread concerns studying the dependence on carbon nanotube diameter in greater detail. Koga et al. examined five tube sizes; subsequent work mapped the phase behavior over a much finer diameter grid, revealing that the n = 4, 5, 6, 7 sequence does not exhaust the possibilities. Octagonal and other ring sizes have been found [4], [10], and the crossover from quasi-1D to quasi-2D behavior (as diameter increases) has been studied systematically [4], [11]. The question of what happens at the extreme of single-file water (one molecule per cross-section) has attracted particular interest because single-file transport is relevant to biological channels such as aquaporins [5], [12].

A third thread is experimental. Direct imaging of ice nanotubes by transmission electron microscopy and X-ray scattering has confirmed the existence of ordered water structures inside nanotubes, with ring sizes consistent with the simulation predictions [13]. Proton NMR and dielectric spectroscopy have provided evidence for solid-like dynamics in the confined phase at temperatures above the bulk melting point. More recent solid-state NMR studies have identified specific ordered water cluster structures in crystalline molecular nanopores [14], showing that the confined-ice concept generalizes well beyond single-walled carbon nanotubes.

The pressure and mechanics of confined phases constitute a fourth active area. Understanding a first-order phase transition in confinement requires knowledge of the local pressure environment - a technically challenging problem because the microscopic pressure tensor is not uniquely defined. Shi et al. [15] addressed this for cylindrical geometries: they derived the local pressure tensor in cylindrical coordinates, accounting for the long-range Coulombic contribution via a Harasima/Ewald method, and applied it to calculate the axial pressure profile of water inside a (20,20) carbon nanotube. The study found that confined water is in an overall stretched state in the axial direction - a result that illuminates why the freezing transitions observed in [1] are accessible at the moderate pressures studied. Building on that, Shi et al. examined the coarse-grained tangential pressure in slit-pore geometries [16] and provided a broader perspective on the microscopic pressure tensor and its connections to high-pressure phenomena in confined nanophases [17]. Related work examined pressure enhancement in slit pores as a function of molecular shape and fluid-wall interaction strength [18].

A fifth direction connects the Koga et al. paper to frontier work in quasi-1D physics. Ising's theorem on the absence of phase transitions in 1D at finite temperature [2] applies only to classical systems with short-range interactions. In quantum systems the picture is richer: quantum fluctuations can stabilize or destabilize ordered phases, and the pre-critical region above the T = 0 K “critical point” can exhibit strong long-range correlations in measurable properties such as the specific heat. Our recent work [19] reports path-integral Monte Carlo results for 1D Lennard-Jones fluids, showing that the correlation length diverges as T approaches 0 K and the specific heat also diverges on approach to this "critical point", with the caveat that it must rapidly go to zero at 0 K according to the third law of thermodynamics. These results are relevant to one-dimensional van der Waals materials and can be seen as a quantum-mechanical counterpart to the semi-classical arguments implicit in the Koga et al. critical-point discussion.

The nanofluidics literature has also been heavily influenced by the Koga et al. work [20]. The promise of nanotube-based membranes for water desalination and ultrafast transport depends on understanding the phase state of water in the pore [20], [21]: is it liquid-like (mobile) or solid-like (frozen)? The rich phase diagram revealed by Koga et al. shows that this question cannot be answered without knowing both the tube diameter and the applied pressure, and that under certain conditions confined water can become solid at room temperature [13], [22]. Conversely, the hollow-tube solid phases may enable highly ordered, defect-controlled ion channels [23], [24].

The broader confined-phase-transition literature has also drawn heavily on [1] as a benchmark. Work by Hung et al. [25], [26] on freezing of simple fluids (Lennard-Jones CCl_4) inside multi-walled carbon nanotubes found a qualitatively different phase behavior: concentric layers freezing into quasi-two-dimensional hexagonal crystals with defects, with outer layers freezing above and inner layers below the bulk melting point. The contrast with the quasi-1D behavior in [1] is instructive: the quasi-2D freezing seen in larger nanotubes reflects the competition between fluid-wall and fluid-fluid interactions, whereas the quasi-1D ice nanotubes of [1] reflect the extreme geometric constraint of near-single-file confinement.

Open questions and future directions

Despite more than two decades of follow-on work, several questions raised or suggested by [1] remain incompletely answered.

The role of quantum nuclear motion is perhaps the most fundamental. The TIP4P and similar models treat water nuclei classically. The hydrogen nucleus is light enough that quantum zero-point motion contributes non-negligibly to structural and thermodynamic properties, particularly at low temperatures. Path-integral simulations of water in nanotubes have been performed, and they show that quantum effects shift the phase boundaries somewhat [8], but a full picture of how the ice nanotube phase diagram is modified by quantum effects is still lacking. Such studies would help in elucidating whether quantum effects are responsible for deviations from experimentally observed freezing transitions in small nanotubes [27]. The machinery for such calculations is now well established, as demonstrated for 1D fluids in [19], and its systematic application to nanotube-confined water would be a valuable contribution.

The question of how defects and disorder interact with the ordered nanotube phases is also important for connecting simulation to experiment. Koga et al. noted that the hexagonal ice nanotube could accommodate helical defects while retaining overall long-range order. How robust are these phases to more severe disorder, *e.g.* to chemical defects in the nanotube wall, the presence of ions, or the corrugated potential of a real atomistic tube? Recent simulations show that carbon nanotube polarization and stacking geometry significantly affect the structural and dynamical properties of confined water [28], suggesting that the smooth-wall approximation may miss important physics in narrower tubes. Similar evidence has found an important impact of chemical functionalization of the nanotube wall [29].

Machine-learned interatomic potentials represent one of the most exciting methodological developments since 2001. Neural-network and other machine-learned potentials can reproduce the accuracy of ab initio density functional theory while incurring the computational cost of a classical force field. For water, several high-quality machine-learned potentials are now available. Their application to nanotube-confined water, where the correct description of both water-water hydrogen-bond energy and the geometry-dependent water-carbon interaction is crucial, is an active area [8], [30] that promises to resolve remaining quantitative uncertainties in the phase diagram.

From a fundamental perspective, the solid-liquid critical point remains the most profound and under-explored prediction of [1]. The theoretical framework for such critical points in quasi-1D systems is not fully developed, and it is not clear whether the critical point predicted by Koga et al. belongs to a known universality class or constitutes a genuinely new type of critical behavior. Connecting it rigorously to the Ising model critical point at T = 0 K, accounting for the tube geometry and the quantum nature of the water molecules, is a fundamental problem including statistical mechanics, quantum mechanics, and molecular simulation.

Finally, from the experimental side, direct observation of the solid-liquid critical point remains elusive. The predicted critical point lies around 280-300 K and 200-300 MPa - conditions achievable in principle but challenging to realize inside a nanotube of ~0.55 nm inner radius. More fundamentally, mapping the phase boundary near the critical point requires studying tubes whose diameters are controlled to sub-Angstrom precision: the Raman spectroscopy experiments of Agrawal et al. showed that a difference of 0.01 nm between two nominally similar tubes shifts the freezing temperature by tens of degrees [27], meaning that even small uncertainties in diameter wash out the critical features one is trying to resolve. Advances in the synthesis of ultranarrow, defect-free nanotubes with well-characterized chirality, combined with improved X-ray and neutron scattering techniques for probing structure in confined phases, may eventually make this experiment possible

Concluding remarks

The 2001 paper by Koga, Gao, Tanaka, and Zeng is a landmark in the molecular simulation of confined systems. In four densely packed pages, it demonstrated that water confined in single-walled carbon nanotubes of sub-nanometer diameter forms entirely new quasi-one-dimensional ice phases with no bulk analogue, that the first-order vs. continuous character of the phase transition depends sensitively on tube diameter and pressure, and that a solid-liquid critical point (a phenomenon thermodynamically forbidden in three dimensions) may exist in this quasi-1D system. These findings established a rich research program that continues to the present day, encompassing the mechanics of confined nanophases, nanofluidic transport, quantum effects in low-dimensional materials, and the development of better molecular models. More than a thousand subsequent papers attest to the depth and breadth of its influence. It deserves recognition as one of the founding papers of nanoscale phase-transition physics.

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