The press coverage of my research

[Jaeil Bai, The University of Nebraska]

J. Bai, J. Wang, and X.C. Zeng "Multiwalled ice helixes and ice nanotubes," The **Proceedings of the National Academy of Science of the USA [PNAS]** 103, 19664-19667 (2006). [Featured in Earth & Sky Radio Show , American Scientist (The Magazine of Sigma Xi Scientific Research Society) , Royal Society of Chemistry (England) , Nature May 31, 2007 , Nature Nanotechnology Jan. 5, 2007 , New Scientist Dec. 12, 2006 , The Science Coalition , Science Daily , Lincoln Journal Star - Dec. 13, 2006 , Nanotechnology World , ZDNet , Materials gate , Nano Werk , Mad Cow News Site , Physorg , Newswise , Azo-nano , Sufficiently advanced , Innovations Report (Germany) , Nanotechwire , EurekAlert , What's Next In Science & Technology , Cogito.org , CCNews , Abrahadabra , Roland Piquepaille's Technology Trends , Metareligion

---

J. Bai, X.C. Zeng, H. Tanaka, and J.Y. Zeng, " Metallic single-walled silicon nanotubes, " The **Proceedings of the National Academy of Science of the USA [PNAS]** 101, 2664-2668 (2004). Reported in UNL Newspaper - Scarlet . Also featured by Intute Spotlight , by BETTERHUMANS , by NewsWise , by Magazine of American Society ofMechanical Engineers , by Materialstoday , by SMALL , and by Advanced Materials & Processes (ASM Inter national), May 2004

---

* **J. Bai**, C.A. Angell, and X.C. Zeng "Guest-free monolayer clathrate and its coexistence with two-dimensional high density ice," The **Proceedings of the National Academy of Science of the USA [PNAS]** 107, 5728-5722 (2010) [Featured in Scarlet, UNL News paper].

nature nanotechnology

Journal content
Journal home
Advance online publication
Research Highlights
Current issue
Archive
Press releases

Journal information
For authors
Online submission
For referees
About the journal
Pricing
Contact the journal

Research Highlights

Nature Nanotechnology Published online: 5 January 2007 | doi:10.1038/nnano.2007.3

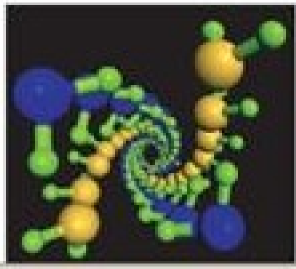
Subject Categories: Carbon nanotubes and fullerenes | Computational nanotechnology

Nanostructures: On thin ice

Stuart Cantrill

Computer modelling reveals that water molecules confined inside carbon nanotubes freeze under high pressure to form helical ice sculptures

Although relatively small and quite simple in terms of their composition, water molecules crystallize into a diverse range of ordered structures in the solid state. Ice crystals are held together by strong intermolecular interactions, known as hydrogen bonds, between the hydrogen and



Subscribe to Nature Nanotechnology
Subscribe

Language selector
Kanji abstract for this article

This issue
Table of contents
Previous article
Next article

Article tools
Send to a friend
Export citation
Export references

Research Highlights

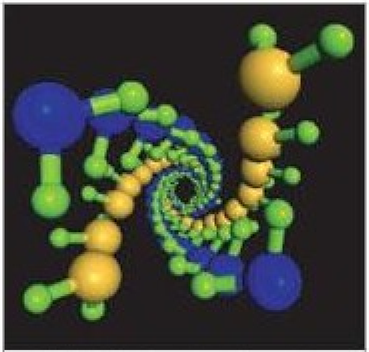
Nature Nanotechnology Published online: 5 January 2007 | doi:10.1038/nnano.2007.3

Subject Categories: Carbon nanotubes and fullerenes | Computational nanotechnology

Nanostructures: On thin ice

Stuart Cantrill

Computer modelling reveals that water molecules confined inside carbon nanotubes freeze under high pressure to form helical ice sculptures



Although relatively small and quite simple in terms of their composition, water molecules crystallize into a diverse range of ordered structures in the solid state. Ice crystals are held together by strong intermolecular interactions, known as hydrogen bonds, between the hydrogen and oxygen atoms of adjacent molecules.

When water freezes in a confined space — such as inside a carbon nanotube — structures very different to those observed in the bulk are formed. Now, Xiao Zeng and co-workers[1] from the University of Nebraska in the USA have studied the effects of pressure on this process. A series of simulations were performed in which water molecules were located inside a nanotube and pressure was applied at each end as the temperature was lowered. In each case, helical arrangements of water molecules were observed, with the precise structure depending on the diameter of the nanotube in question and the magnitude of the applied pressure. Double-walled assemblies were observed in smaller tubes, whereas triple-walled structures formed inside the larger ones.

This study allows the fluid properties and phase transitions of one of the most well known substances to be investigated at the nanoscale. Moreover, it demonstrates that the beauty of ice crystals does not depend on scale — the structures unveiled in this study are as pretty as any snowflake.

REFERENCES

top

1. Bai, J., Wang, J. & Zeng, X. C. Multiwalled ice helixes and ice nanotubes. *Proc. Natl Acad. Sci. USA* **103**, 19664–19667 (2006). | Article |

NACHRICHTEN & BERICHTE
Agrar- Forstwissenschaften
Architektur Bauwesen
Automotive
Biowissenschaften Chemie
Energie und Elektrotechnik
Geowissenschaften
Gesellschaftswissenschaften
Informationstechnologie
Interdisziplinäre Forschung
Kommunikation Medien
Maschinenbau
Materialwissenschaften
Medizintechnik
Medizin Gesundheit
Ökologie Umwelt- Naturschutz
Physik Astronomie
Studien Analysen
Verfahrenstechnologie
Verkehr Logistik
Wirtschaft Finanzen

Home → Fachgebiete → Biowissenschaften Chemie → Nachricht

Self-assembling nano-ice discovered at UNL; structure resembles DNA

14.12.2006 › nächste Meldung ›

Working at the frontier between chemistry and physics, the University of Nebraska-Lincoln's Xiao Cheng Zeng usually finds his reward in discovering the unexpected through computer modeling.

Zeng and his colleagues regularly find new and often unanticipated behaviors of matter in extreme environments, and those discoveries have been published several times in major international scientific journals. Their findings, though, have been so far ahead of existing technology that their immediate practical impact was essentially nil -- until now.

Zeng and two members of his UNL team recently found double helixes of ice molecules that resemble the structure of DNA and self-assemble under high pressure inside carbon nanotubes. This discovery could have major implications for scientists in other fields who study the protein structures that cause diseases such as Alzheimer's and bovine spongiform ecephalitis (mad cow disease). It could also help guide those searching for ways to target or direct self-assembly in nanomaterials and predict the kind of ice future astronauts will find on Mars and moons in the solar system.

Zeng, post-doctoral student Jaeil Bai and doctoral candidate Jun Wang reported their findings in the Dec. 11-15 online edition of the Proceedings of the National Academy of Sciences.

neuronal proteins. For several, the method could pin-point the position of the added sugar. They also found that some proteins showed more *O*-GlcNAc modifications if they were taken from an intact brain shortly after its neurons had been stimulated than if they were taken from unstimulated brain tissue.

ASTRONOMY

Universal dust-up

Astrophys. J. **661,** L9–L12 (2007)

The most distant γ-ray burst ever seen has cast its light on dust in the early Universe.

Giulia Stratta of the ASI Science Data Center in Frascati, Italy, and her colleagues studied the radiation from a 12.8-billion-year-old burst over three days. The emission was fainter at certain wavelengths than expected from the burst's initial brightness, suggesting that dust in the early Universe is different to that found in the Universe today.

Dust is produced in the dying explosions of stars, so the amount of dust present at this early time and its composition could provide clues about how the first stars formed.

CHEMISTRY

The simplest link

Science **316,** 1172–1175 (2007)

It is now possible to join certain ring-shaped molecules together without resorting to chemical tinkering to make them more reactive. This provides a simple way to perform 'cross-coupling' reactions, a type of reaction widely used in the drug industry.

David Stuart and Keith Fagnou from the University of Ottawa, Canada, used a palladium and copper catalyst system to build carbon–carbon bonds between benzene and two-ringed molecules known as indoles.

Cross-coupling reactions have previously required several steps, with the starting materials first being converted into more reactive analogues. In the new scheme, the catalyst activates a carbon–hydrogen bond on the indole, making it reactive enough to form a bond with one of the benzene's carbon atoms. There are no unwanted side products.

CANCER BIOLOGY

Stem cells fished out

Genes Dev. doi:10.1101/gad.1545007 (2007)

A model of a common and often fatal childhood cancer — embryonal rhabdomyosarcoma (ERMS) — may have helped researchers to identify the stem cells that mediate the disease.

Leonard Zon of the Children's Hospital Boston in Massachusetts and his colleagues induced ERMS in zebrafish by activating a signalling pathway that is mediated by the Ras protein. This pathway is commonly activated in human ERMS, the researchers found.

They identified genetic pathways that drive progression of the disease in both zebrafish and humans, and found that tumour development in the zebrafish depends on a population of cancer stem cells. These cells triggered tumour development when transplanted into healthy animals. The human counterparts may be 'activated satellite cells', found in muscle. Gene-expression studies showed these to have similar self-renewal mechanisms to the zebrafish cancer stem cells.

T. BLACKALL

NITROGEN CYCLE

Seabirds add ammonia

Geophys. Res. Lett. **34,** L10801 (2007)

Seabird colonies are the world's largest point sources of atmospheric ammonia, according to new calculations.

Trevor Blackall, now at King's College London, and his colleagues travelled to two Scottish islands — the Isle of May, home to a colony of Atlantic puffins, and Bass Rock (pictured above), which houses thousands of Northern gannets — to measure how much of the gas is released by bird droppings.

Globally, birds' ammonia emissions are outstripped by those from livestock, synthetic fertilizers and oceans. But the researchers estimate that, in the relatively pristine Southern Ocean below 45° S, penguins account for almost 20% of ammonia emissions. The largest colonies may produce up to 6,000 tonnes of ammonia per year, more than even the biggest poultry farms.

JOURNAL CLUB

Iwao Ohmine
Nagoya University, Japan

A theoretical chemist compares love to hydrogen bonds.

Water molecules assemble into ice "palm to palm", like Romeo and Juliet on their first encounter. Each molecule reaches out to four neighbours, forming hydrogen bonds that lock the molecules into a tetrahedral network. And like the love of Shakespeare's pair, water's hydrogen bonds are resilient. Ice contrives to keep its network, even in the tightest of spaces.

Researchers recently predicted that ice constrained by a carbon nanotube's wall will form either tubular structures or intricate arrangements of double- and quadruple-stranded helices, depending on temperature, pressure and nanotube diameter (J. Bai *et al. Proc. Natl Acad. Sci. USA* **103,** 19664–19667; 2006).

I have spent many years studying the structure and dynamics of water, but am still amazed by these luxuriant ice structures. Had computer simulations not shown how strenuously ice's network can adapt for its molecules to keep their four hands touching, we could hardly have imagined such structures would be possible.

Simulations have also predicted that confined ice can have two symmetrically different phases, which become deformed and indistinguishable when put under pressure (K. Koga *et al. Nature* **412,** 802–805; 2001). So we expect that one type of ice will easily transform into the other through collective motion of its hydrogen bonds.

My prediction is that confined liquid water, which has a disordered network of hydrogen bonds, will undergo similar structural rearrangements. Molecular mechanisms may cause large changes to the network structure of water trapped in proteins or at membrane surfaces, for example. These studies could therefore help us begin to understand another intimate relationship — the relationship between water and life.

Discuss this paper at **http://blogs.nature.com/nature/journalclub**

About this Magazine

- About Chemistry World
- Prices & Subscriptions
- People & Contacts
- Cover Gallery

Reader Services

- Latest Issue
- Previous Issues
- Jobs
- News
- Regulars
- Features
- Advertising
- Chemistry World Blog
- Send us an email

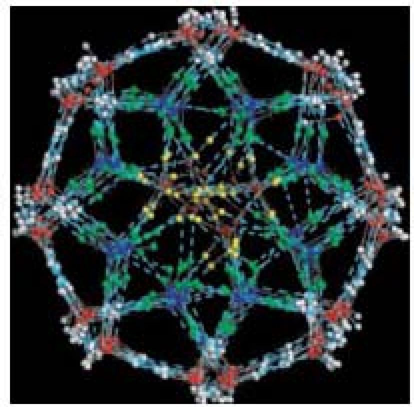
Customer Services

- Sample Content
- Online Access
- Copyright & Permissions

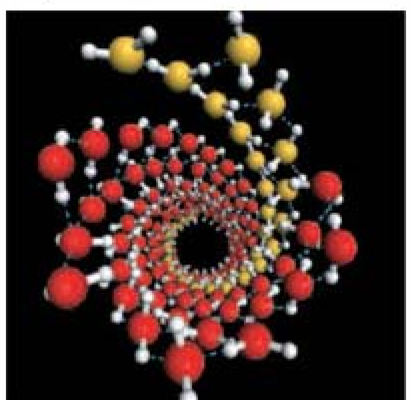
Ice crystals trapped inside nanotubes

18 December 2006

At this time of year there are reminders everywhere of the beautiful structures that water can form when it freezes. But the ice crystals predicted in computer simulations by Xiao Cheng Zeng and colleagues at the University of Nebraska, Lincoln, US, are as striking as any snowflake.[1]



Projected view along the axis of double-walled tubular nanoice formed at 500 MPa
© X C Zeng et al/U. Nebraska/PNAS



The patterns are formed from water freezes under high pressure inside carbon nanotubes. The small width and hydrophobic walls of nanotubes place severe constraints on the

RSC quicklinks

I want information on: Select a subjec

Information for: Select a role

I am interested in: Select a produ

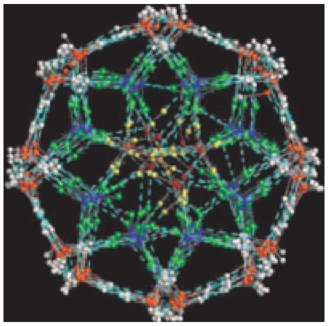
RSC | Advancing the Chemical Sciences

Chemistry World

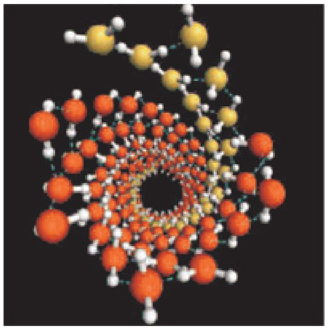
Ice crystals trapped inside nanotubes

18 December 2006

At this time of year there are reminders everywhere of the beautiful structures that water can form when it freezes. But the ice crystals predicted in computer simulations by Xiao Cheng Zeng and colleagues at the University of Nebraska, Lincoln, US, are as striking as any snowflake.[1]



Projected view along the axis of double-walled tubular nanoice formed at 500 MPa
© X C Zeng et al/U. Nebraska/PNAS

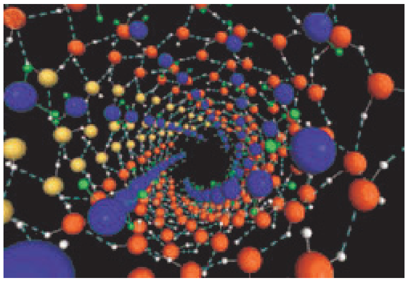


The octuple-stranded nanoice helix consists of four double-helices
© X C Zeng et al/U. Nebraska/PNAS

The patterns are formed from water freezes under high pressure inside carbon nanotubes. The small width and hydrophobic walls of nanotubes place severe constraints on the hydrogen-bonded network of ice, forcing it to adapt in novel ways. So far, several unusual forms of ‘tubular’ ice have been identified inside nanotubes at atmospheric pressure. But since ordinary ice undergoes transformations to complex, denser network structures when compressed, Zeng and colleagues suspected that squeezing ice inside a nanotube – as though between pistons placed at each end – might produce interesting new variants.

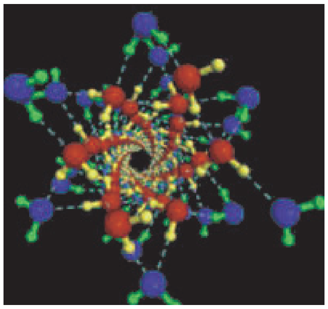
They conducted simulations for four nanotubes with diameters of between 1.35 and 1.9 nanometres, and with different helical windings of the rows of carbon hexagons in the tubes’ wall. Six distinct phases of ‘nano-ice’ appeared at pressures of up to four billion Pascals (4 GPa, or 40,000 atmospheres).

In general, the water molecules arranged themselves into concentric shells, with hydrogen bonds holding together the molecules in each shell. Some of these had helical structures: one consisted of two helical shells, the innermost being a helix of four hydrogen-bonded strands and the outermost a series of four double-helical strands.



Top view of the outer and middle walls of triple-walled nanoice
© X C Zeng et al/U. Nebraska/PNAS

The largest nanotube studied was wide enough to accommodate a triple-shelled ice structure, with the outer shell having 18 helical strands and the inner two shells comprised of 6 strands each.



Top view of the middle and inner walls of triple-walled nanoice
© X C Zeng et al/U. Nebraska/PNAS

With so many new phases from just a small number of confining geometries, it is tempting to conclude that ice may adjust itself in a unique way to just about any nano-environment, rather than simply freezing into the bulk solid as, for example, metals seem to do inside nanotubes. An even more enticing question is whether liquid water might also exhibit some unusual structures in nanotubes – although simulations have suggested that it would, there’s no firm experimental evidence for it yet.

Philip Ball

References

J Bai, J Wang and X C Zeng, *Proc. Natl. Acad. Sci*. 2006, DOI: 10.1073/pnas.0608401104

Scarlet

from the issue of December 14, 2006

Project uncovers DNA-like ice structures

BY TOM SIMONS, UNIVERSITY COMMUNICATIONS

Working the frontier between chemistry and physics, Xiao Cheng Zeng has grown accustomed to discovering the unexpected through computer modeling.

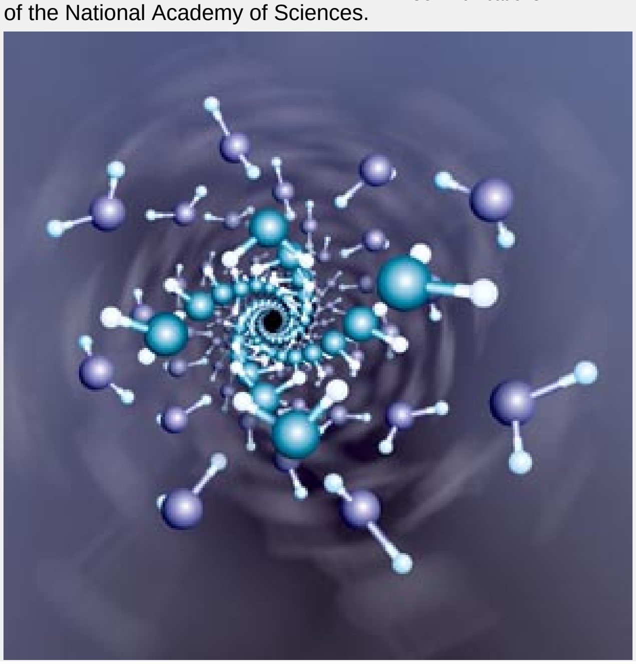
Regularly, Zeng and his colleagues find new - often unanticipated - behaviors of matter in extreme environments. Their discoveries have been published several times in international scientific journals. However, those findings have been ahead of existing technology and immediate practical impact was essentially nil - until now.

RESEARCH GROUP - Members of the UNL research group that discovered the nano-ice double helix are (from left) doctoral candidate Juan Wang, chemistry professor Xiao Zeng and post-doctoral student Jaeil Bai. Photo by Troy Fedderson/University Communications.

Zeng and two members of his team have discovered double helixes of ice molecules. Resembling the structure of DNA, the molecules self-assemble under high pressure in carbon nanotubes.

The discovery could have major implications for scientists in other fields that study protein structures that cause diseases such as Alzheimer's and mad cow. It may also help guide those searching for ways to target or direct self-assembly in nanomaterials and predict the kind of ice that may be found on Mars and moons in the solar system.

Zeng, post-doctoral student Jaeil Bai and doctoral candidate Jun Wang reported the findings in the Dec. 11-15 online edition of the Proceedings of the National Academy of Sciences.



The team found the self-assembling double helix of nano-ice following a months-long experiment on UNL's PrairieFire supercomputer.

The experiment was a follow-up on a 2001 discovery in which Zeng, working with another team, modeled four new kinds of one-dimensional ice inside carbon nanotubes. Scientists elsewhere confirmed through laboratory experiment the existence of three of the new nano-ices. One result in particular intrigued Zeng, Bai and Wang. Scientists at Argonne National Laboratory near Chicago confirmed the existence of a chain of octagon-shaped ice crystals inside a 1.4-nanometer carbon tube, just as Zeng and company expected. But the Argonne group also found an additional, unexpected chain of water molecules.

Zeng said that report inspired another look at one-dimensional ice, but this time with a PrairieFire that was 20 times more powerful that it had been five years earlier. The 2001 results were achieved at atmospheric pressures, but PrairieFire's added processing power enabled Zeng, Bai and Wang to design simulations that greatly increased the pressure on the water molecules.

"We were shocked to see these molecules arrange themselves in this way," said Zeng, university professor of chemistry. "We thought it would be like two tubes, one inside the other, but it didn't do that. It was helical, like DNA. I'm speculating, but maybe the helix is a way for molecules to arrange

COMING TOGETHER - This computer image demonstrates how the nano-ice double helix forms. Oxygen atoms are blue in the inner helix, purple in the outer helix. The hydrogen atoms are white.

themselves in a very compact, efficient way under high pressure.

"This ice formation can be viewed as a self-assembling process, and self-assembly is a way for molecules to bond together through weak hydrogen bonds. One example of a self-assembling material is protein. Proteins can self-assemble into structures like amyloid fibrils that can build up in the brain to cause Alzheimer's disease or prions that cause mad cow disease."

Another implication, Zeng said, is that these self-assembling helical ice structures may give scientists and engineers a different way to think about weak molecular bonds and the self-assembly process as they try to develop ways to direct self-assembly in making new materials.

He said that while scientists have a good understanding of covalent bonds (the strong type of bonding where atoms share electrons), knowledge is not as complete about the weak bonds, such as hydrogen bonds, that are essential to the self-assembly process.

"We're happy to see potential applications that can maybe advance some fundamental science," Zeng said. "We're not engineers in direct contact with technology, but if our research can make some contribution, we're happy."

Zeng and his colleagues achieved their results by running four series of molecular dynamics simulations on PrairieFire and Department of Chemistry computers, using simulated carbon nanotubes ranging in diameter from 1.35 to 1.9 nanometers. They used Earth-like temperatures ranging from 117 degrees Fahrenheit to 9 degrees below zero F., but with pressures ranging from 10 to 40,000 atmospheres, with each series lasting no more than a few 10s of nanoseconds.

Most of the experiments produced the expected tubular structures, but in a simulation in a 1.35-nanometer tube at minus-9 degrees F. and 40,000 atmospheres, the ice transformed into a braid of double helix that resembles DNA in structure and in the weak bonds between the helixes. Additionally, in a simulation in a 1.9-nanometer tube at the same temperature, pressure on the confined liquid water was instantly raised from 10 atmospheres to 8,000. The confined liquid froze spontaneously into a high-density, triple-walled helical structure.

This research was funded by the Department of Energy, the National Science Foundation, the Nebraska Research Initiative and the John Simon Guggenheim Foundation.

GO TO: ISSUE OF DECEMBER 14

NEWS HEADLINES FOR DECEMBER 14

732659S36529X

DNA-like ice 'seen' inside carbon nanotubes

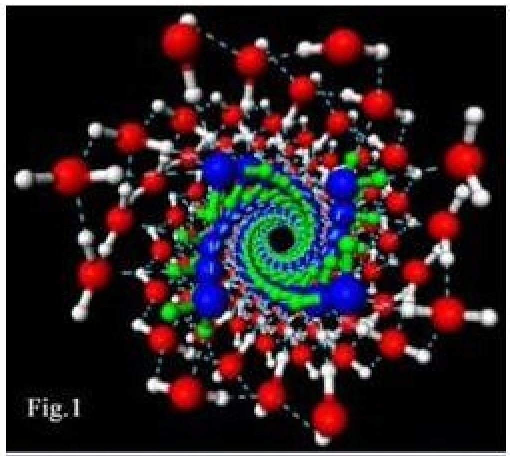
14:15 12 December 2006
NewScientist.com news service
Tom Simonite

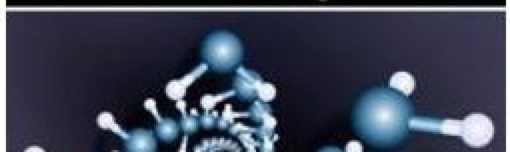
Nanoscale ice formations resembling the double helices of DNA will form when water molecules are frozen inside carbon nanotubes, detailed computer simulations suggest.

Researchers at the University of Nebraska, US, used a supercomputer to run detailed mathematical models of the behaviour of water molecules. In their simulations, they inserted the molecules into carbon nanotubes under high pressure, before cooling them to -23°C.

The scientists were surprised to see the molecules organise themselves into "spiral staircase" arrangements similar to those of a DNA helix. "It was very unexpected," Xiao Cheng Zeng, the computational nanotechnology expert who led the research told **New Scientist**. "We had expected ice to form into tube structures that have been observed before inside carbon nanotubes."

The simulations involved modelling the behaviour of water molecules packed inside nanotubes measuring between 1.35 and 1.9 nanometres in diameter, under pressures of 10 to 40,000 atmospheres. The combination of such a confined environment and such extreme pressures distorted the hydrogen bonds within each water molecule in ways never seen before. Zeng





DNA-like ice 'seen' inside carbon nanotubes

14:15 12 December 2006
NewScientist.com news service
Tom Simonite

Nanoscale ice formations resembling the double helices of DNA will form when water molecules are frozen inside carbon nanotubes, detailed computer simulations suggest.

Researchers at the University of Nebraska, US, used a supercomputer to run detailed mathematical models of the behaviour of water molecules. In their simulations, they inserted the molecules into carbon nanotubes under high pressure, before cooling them to -23°C.

The scientists were surprised to see the molecules organise themselves into "spiral staircase" arrangements similar to those of a DNA helix. "It was very unexpected," Xiao Cheng Zeng, the computational nanotechnology expert who led the research told **New Scientist**. "We had expected ice to form into tube structures that have been observed before inside carbon nanotubes."

The simulations involved modelling the behaviour of water molecules packed inside nanotubes measuring between 1.35 and 1.9 nanometres in diameter, under pressures of 10 to 40,000 atmospheres. The combination of such a confined environment and such extreme pressures distorted the hydrogen bonds within each water molecule in ways never seen before, Zeng says.

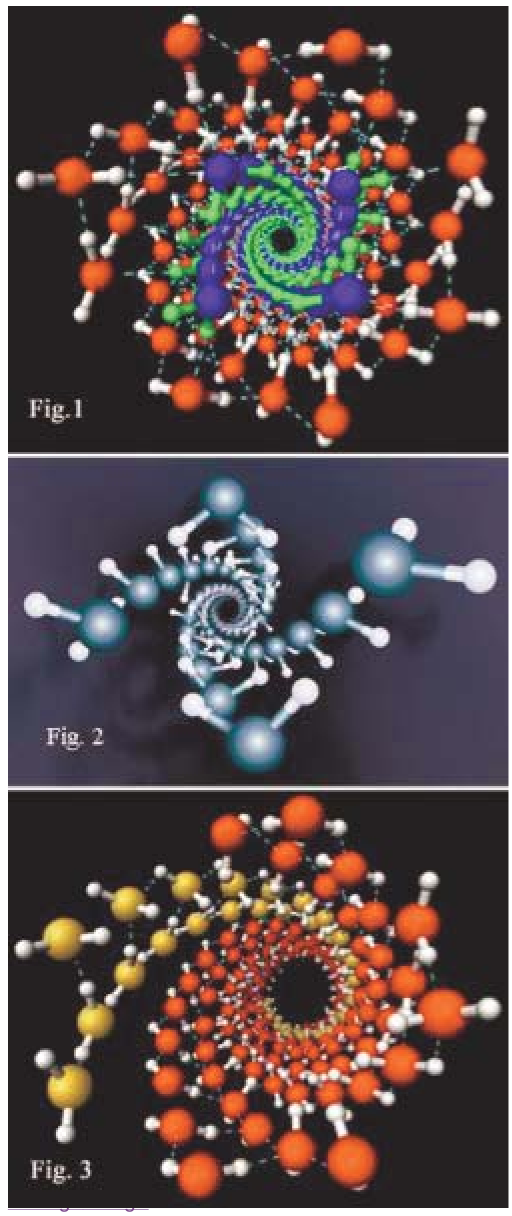
Spectacular sight

Under most conditions the simulated molecules formed the expected tubular structures. However, those in which water was squeezed into a 1.35-nm-diameter nanotube at around 40,000 atmospheres of pressure saw ice form into a spectacular double walled ice helix (Fig. 1, right).

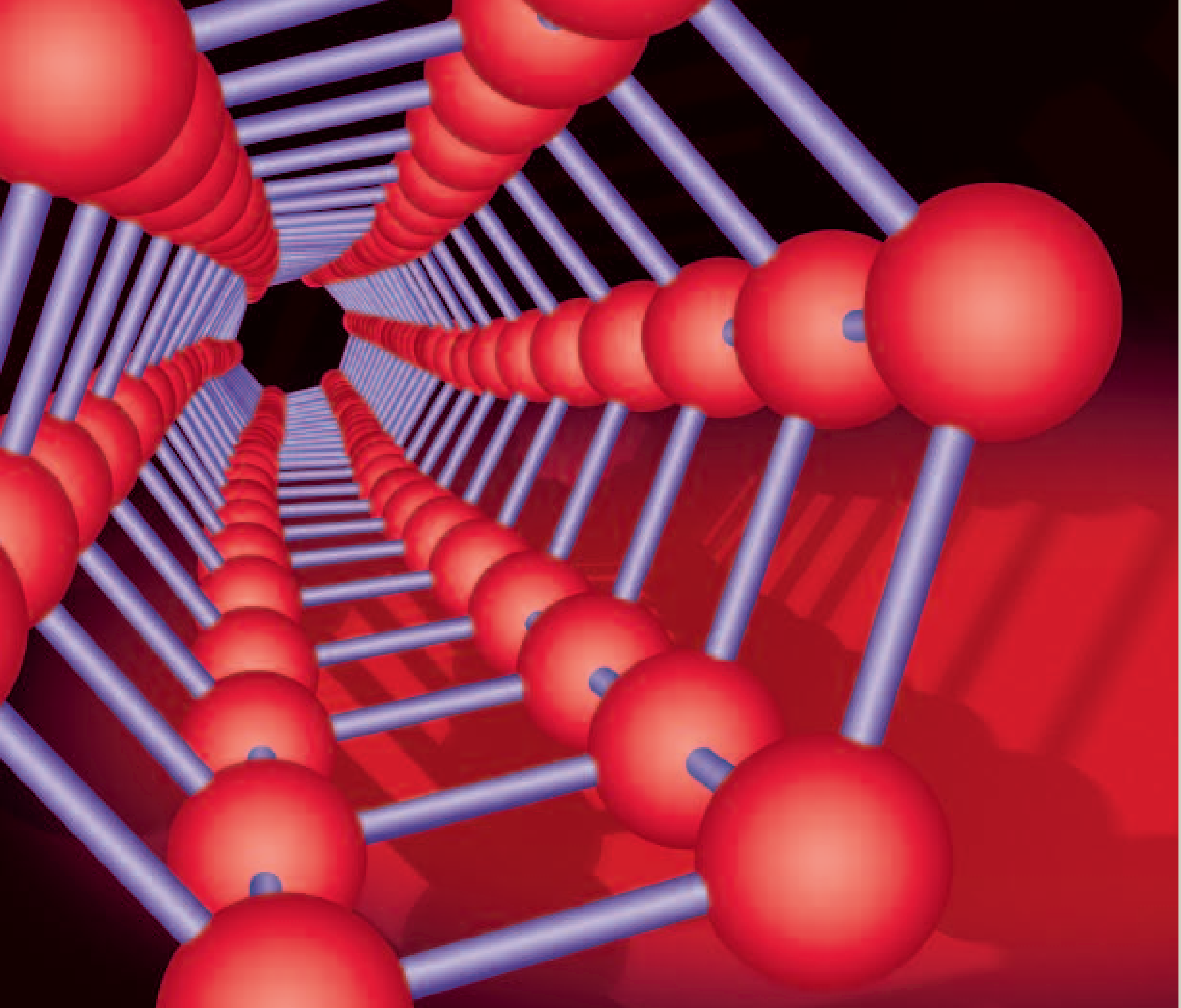
The inner wall is a four-stranded helix (Fig. 2) and the outer wall consists of four double-stranded helices, each also resembling a DNA double helix (Fig. 3).

Zeng was part of a team that previously discovered the formation of tiny tubes of ice inside carbon nanotubes in 2001, confirming computer simulations performed several years earlier. "I expect these new predictions to also be confirmed," Zeng adds. "Experimental researchers can use infrared spectroscopy or neutron scattering to look for these new structures."

Journal reference: *Proceedings of the National Academy of Sciences*



Spectacular ice helix structures form when water molecules are squeezed into carbon nanotubes under high pressure, in computer simulations (Images: Xiao Cheng Zeng)



UNIVERSITY OF Nebraska Lincoln

Office of Research & Graduate Studies

ANNUAL REPORT 2003/2004

Silicon behaves like metal when formed into nanotubes

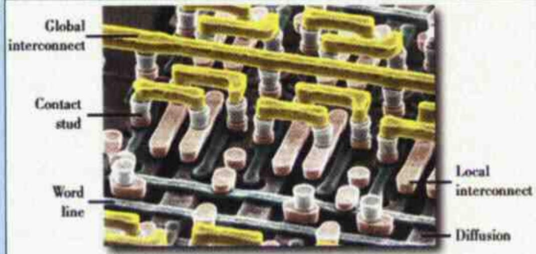
When silicon is shaped into tubes less than 1 nm in diameter, it may behave like a metal, reports University of Nebraska-Lincoln. Prof. Xiao Cheng Zeng and his team modeled nanotubes in hexagonal, pentagonal, and square configurations on the university's powerful supercomputer (PrairieFire). They found the thinnest known nanotube has a square configuration with a diameter of less than 0.5 nm.

The researchers then used a quantum mechanical method to analyze the tubes and found that they are very likely to be conductors. In other words, they appear not to have the semiconducting properties that have made three-dimensional silicon one of the foundation materials for the modern electronics industry.

"To find that these tubes are very likely to be metals instead of semiconductors is very surprising," says Dr. Zeng. "Scientists have studied silicon for more than 50 years and it's the cornerstone material for the modern semiconductor industry."

For more information: Dr. Xiao Cheng Zeng, University of Nebraska – Lincoln, NE 68588; tel: 402/472-9894; e-mail: xzeng@unniserve.unl.edu; Web site: www.Nebraska.edu.

Highways on a chip



This low-angle scanning electron micrograph shows a portion of a partially completed array of SRAM (static random access memory) containing six-device memory cells. The insulating oxide films have been removed, revealing the lower levels of the interconnect structure. The word lines are colored green and are made of salicided polysilicon. The yellow lines are global interconnects, and are made of Ti/AlCu/Ti/TiN. The pink interconnects and the gray plugs are made of tungsten, which is applied as tungsten metal, tungsten silicide, tungsten nitride, and tungsten-titanium alloy thin films. This image is from www-3.ibm.com/chips/technology. For more information: International Tungsten Industry Association, 2 Baron's Gate, 33 Rothschild Road, London, England W4 5HT; tel: 44 20 8742-2274; fax: 44 20 8742-7345; Web site: www.itia.info.

Light-activated molecules create complex microstructures

A three-dimensional microfabrication technique in which light-activated molecules selectively initiate chemical reactions within polymers and other materials has been reported by researchers at the Georgia Institute of Technology, Atlanta. The technology could provide an efficient way to produce complex structures with sub-micron features. Known as "two-photon 3D lithography," the technique could compete with existing processes for fabricating microfluidic devices, optical storage devices, and micromachines.

Prof. Seth Marder says that the technique is based on a family of organic dye molecules known as bis-donor phenylene vinylenes. These molecules have a special ability to absorb two photons of light simul-taneously. Energized molecules transfer an electron to form a simple acid or a radical group that can initiate a chemical reaction, such as polymer cross-linking or ion reduction.

The reaction begins by adding small concentrations (0.1%) of the molecules to a resin slab containing cross-linkable acrylate monomer. A focused near-infrared laser beam draws patterns and initiates cross-linking reactions only in material exposed to the narrow laser beam. Those areas are then insoluble, allowing the remainder to be washed away to leave a complex three-dimensional structure.

For more information: Prof. Seth Marder, Georgia Institute of Technology, Atlanta, GA 30308; tel: 404/385-6048; e-mail: seth.marder@chemistry.gatech.edu; Web site: www.gatech.edu.

Scarlet

from the issue of March 11, 2004

Study: Silicon can act like metal

BY TOM SIMONS, UNIVERSITY COMMUNICATIONS

Using one large computer, one borrowed graduate student, one good friend and one piece of advice from dear old Dad, a UNL chemist and his team came up with an unexpected discovery: At extremes of size, silicon may behave like a metal.

UNL Chemist Xiao Cheng Zeng, left, and graduate student Jail Bai stand next to UNL뮐 supercomputer PrairieFire, which helped them create models of silicon tubes less than a nanometer in diameter. The models showed that the tubes are likely to be conductors. Photo by Brett Hampton.

Xiao Cheng Zeng and his team used UNL's supercomputer, PrairieFire, to create models of silicon tubes less than 1 nanometer in diameter (that is, less than one-billionth of a meter, essentially making them one-dimensional structures with length but virtually no thickness).

They modeled nanotubes in hexagonal, pentagonal and square configurations and in the process, they found the thinnest known nanotube - the square configuration at less than 0.5 nanometer in diameter. More importantly, when they used the quantum mechanical method to analyze the tubes, they found that they are very likely to be conductors. In other words, they appear not to have the semiconducting properties that have made three-dimensional silicon one of the foundation materials for the modern electronics industry.

The result was published in the Feb. 23 issue of the Proceedings of the National Academy of Sciences, one of the world's three leading scientific journals, with Nature and Science.

"To find that these tubes are very likely to be metals instead of semiconductors is very surprising," Zeng said. "Scientists have studied silicon for more than 50 years and it's the cornerstone material for the modern semiconductor industry."

The PNAS paper is the third Zeng and his friend, Hideki Tanaka of Okayama University in Japan, have had published in one of the major journals in a little more than three years, following two on low-dimensional water and ice in Nature in 2000 and 2001. And it was while discussing the earlier papers with his father, J.Y. Zeng, a retired professor of quantum physics at Beijing University in China, that Zeng became interested in the quantum systems that led to the most recent discovery.

"Three years ago, when I visited my dad, I talked about these water studies," Zeng said. "He had studied low-dimensional quantum effects and suggested that I look in that direction. In our work with water and ice, we used the classical physical model without considering quantum effects."

Considering quantum effects proved to be crucial in the work on silicon nanotubes, but first Zeng needed the assistance of someone with a solid background in solid-state and quantum physics. Zeng is a computational and theoretical physical chemist with the title of Willa Cather professor of chemistry at UNL. But he also has a courtesy appointment in the Department of Physics and Astronomy, which allowed him to hire a graduate student with the necessary background: Jail Bai, a doctoral candidate from South Korea and the lead author of the PNAS paper.

Bai joined Zeng's lab in 2001 and for nearly three years, they attacked the problem of understanding the sub-atomic behavior of the tiny silicon tubes, finally achieving success last year.

"Bai used the quantum mechanical method to study the problem and from that study we found that these nanotubes are really quite stable - and we found that these tubes are very likely to be metals instead of semiconductors," Zeng said. "Only quantum physics can tell you the correct behavior of electrons in the nanostructure, and it is the electronic structure that determines whether a material is a metal or a semiconductor. So quantum physics was critical to this."

Another essential element, Zeng said, was the PrairieFire supercomputer, one of the most powerful on a university campus in the United States.

"These experiments took more than a year on PrairieFire," he said. "We would have needed more than six on a PC, and that's beyond a graduate student's 'lifetime.'"

Zeng said he's hopeful that experimental chemists will be able to reproduce his and Bai's model in the laboratory, but he acknowledged that it will be difficult. Creating nanoscale tubes is commonplace in modern labs, but getting silicon into the tubes will be the problem, he said. The element not only has a high melting point at more than 1,600 degrees Kelvin (more than 2,800 degrees Fahrenheit), but it's also highly reactive at high temperatures, making it difficult to work with.

He also said it's far too early to predict what practical uses the tubes might eventually serve. But silicon itself wasn't isolated as an element until 1824 and it was more than a century after that before its value in electronic circuits was understood.

"We're just very gratified to find this new nanostructure three years after we entered the field," Zeng said.

GO TO: ISSUE OF MARCH 11

NEWS HEADLINES FOR MARCH 11

Study: Silicon can act like metal
Area takes holistic view of survey
Facility to work on Valley Fever vaccine
Site features state뭘 fossils
Sociology focuses on building on department뭘 strengths
5 areas added to 멶rograms of Excellence?/a>
Addressing water뭘 legal issues

731651S32998X

Unexpected properties

NANOTECHNOLOGY

Atomistic computer simulations indicate that it could be possible to create one-dimensional Si nanotubes with diameters as small as 0.5 nm [Bai *et al.*, *Proc. Natl. Acad. Sci. USA* (2004) **101**, 2664]. But more surprisingly, *ab initio* calculations indicate that such Si nanostructures could be metals rather than wide band gap semiconductors.

Xiao Cheng Zeng of the University of Nebraska, together with colleagues from Okayama University, Japan and Peking University, China, modeled hexagonal, pentagonal, and square configurations of single-walled Si nanotubes. Even though low-dimensional structures are known to have properties different from the bulk, the results were unexpected. "To find that these tubes are very likely to be metals instead of semiconductors is very surprising," says Zeng.

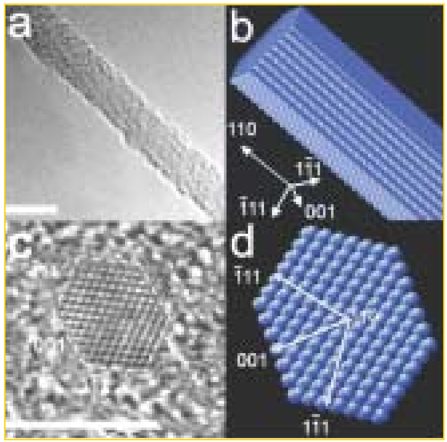
The unusual characteristics of the nanotubes could be a result of their distinct local geometry, which is different from that of cubic diamond Si (the usual bulk structure) or the surface-passivated one-dimensional nanowires produced to date. These experimentally produced nanowires all assume either the bulk structure or that of amorphous Si. Nanowires also tend to have wider band gaps than bulk Si. The nanotubes that Zeng and coworkers have simulated also differ from other hypothetical one-dimensional structures, which have been based on carbon-nanotube-like structures.

Zeng accepts that the ultimate confirmation of their calculations must await experimental proof, but believes that it is possible to fabricate such nanotubes. It is also too early, he says, to suggest possible uses of such one-dimensional metallic structures.

Cordelia Sealy

Smallest diameter nanowires to date

NANOTECHNOLOGY



(a) Transmission electron micrograph (TEM) of 3.8 nm Si nanowire grown along <110> direction; (c) High-resolution TEM of cross-section; (b) and (d) show simulations of the nanowire lattice. Scale bars are 5 nm. (©2004 American Chemical Society.)

Charles M. Lieber and his team at Harvard University have achieved the smallest diameter Si nanowires by direct growth to date [Wu *et al.*, *Nano Lett.* (2004) DOI: 10.1021/nl035162i]. "Such molecular diameter nanowires could exhibit novel properties distinct from materials studied to date," says Lieber.

Using chemical vapor deposition with Au nanoclusters as catalysts and silane as the vapor-phase reactant, the researchers produced nanowires with diameters as small as 3 nm. This is just ten atoms wide and about the same size as a DNA molecule, says Yue Wu. The monodisperse, molecular-scale, single-crystal Si nanowires can be grown in a controllable manner. Transmission electron microscopy examination of the nanowires reveals that the crystallographic growth direction depends strongly on the wire diameter, which can be explained in terms of surface energetics. For the first time on this scale, the researchers show that the surface energetic effect drives a faceting of the nanowire to produce a hexagonal cross-section. Furthermore, the nanowires show no visible amorphous oxide, which the researchers believe is the result of surface passivation by the hydrogen used as a carrier gas during growth.

"These nanowires are opening up unique opportunities for fundamental physics and high-performance devices," Lieber told *Materials Today*. The nanowires could be used to create electronic devices for small, ultrafast computers and memories.

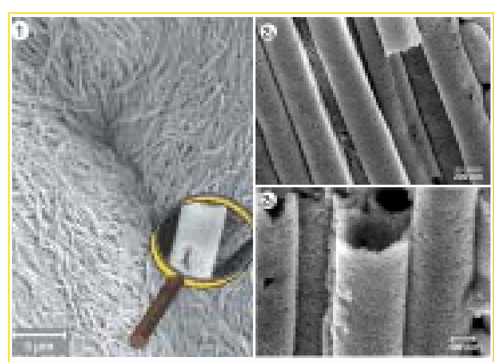
Cordelia Sealy

A new type of tube

NANOTECHNOLOGY

Researchers from the Weizmann Institute of Science, Israel have developed a novel synthetic route for a new type of metal nanotube [Lahav *et al.*, *Angew. Chem. Int. Ed.* (2003) **42**, 5576]. The cylindrical nanotubes are built up from individual metal nanoparticles using a room temperature, three-stage process. A metal colloid solution is first passed through the pores of a nanoporous alumina membrane, the surface of which has been modified with silane. The nanoparticles (in this case Au) are immobilized on the pore walls, creating solid, multilayered nanotubes. Dissolution of the alumina membrane leaves freestanding Au nanotubes. Other metal nanotubes could be made in the same way.

"We were amazed when we discovered the beautifully formed tubes," says Israel Rubinstein. "We expected the nanoparticles to bind to the aluminum oxide template – that has been done before – but we did not expect them to bind to each other, creating the tubes."



(1) Scanning electron micrograph of Au nanoparticle nanotubes; (2a) composite Au/Pd (1:1) nanotubes; and (2b) enlargement of individual Au/Pd nanotube showing the multilayered, hollow structure.

The unique combination of high surface-to-volume ratio, mechanical stability, electrical conductivity, and surface plasmon optical absorption could be useful in catalysis, sensing, and microfluidics.

Cordelia Sealy

University of Nebraska–Lincoln

UNL News Releases

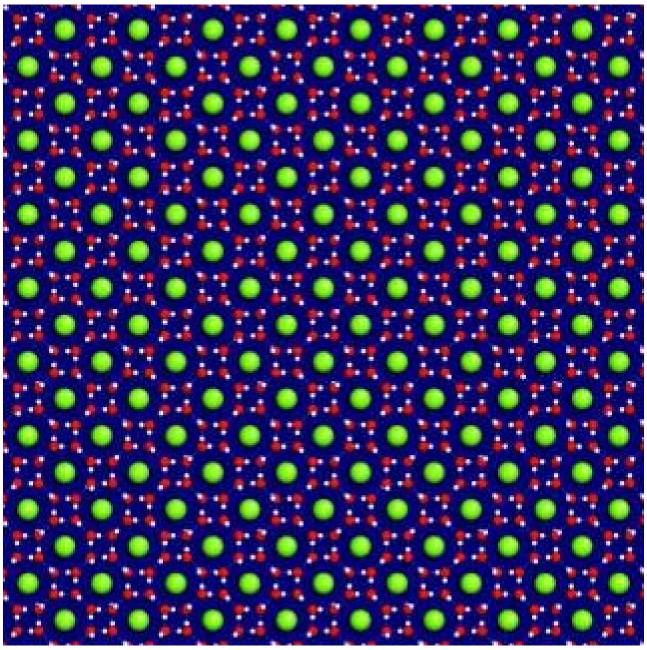
Encounter leads to new ice discoveries by UNL team

Released on 03/25/2010, at 2:00 AM

Office of University Communications
University of Nebraska–Lincoln

Lincoln, Neb., March 25th, 2010 —

Xiao Cheng Zeng (left) and Jaeil Bai



Square-octagon ice clathrate with argon atoms (green) inside octagonal openings

Sometimes in science, new research pathways are generated by unexpected suggestions.

That's what led Xiao Cheng Zeng and his research group at the University of Nebraska-Lincoln to their latest series of discoveries about the behavior of materials -- especially water -- at extremes of temperature, pressure and confinement.

Zeng gave a talk in 2008 to the Materials Research Society in San Francisco about some of his lab's earlier discoveries, including the two-dimensional, high-density "Nebraska ice" that he named for its flatness. After the talk, C. Austen Angell, professor of chemistry and biochemistry at Arizona State University, approached Zeng and suggested that it would be possible to have a two-dimensional ice clathrate with the "Nebraska ice." A clathrate is essentially a molecular cage, usually three-dimensional in nature, in which molecules of one substance are completely enclosed in the crystal structure of another.

The suggestion got Zeng's attention, especially since Angell is regarded as one of the world's foremost experts in liquid physics. When he returned to Lincoln, Zeng asked Jaeil Bai, research technologist in his lab, to create a computer simulation to test the idea. Bai's experiment led to a series of discoveries that were reported in the March 15-19 online edition of the Proceedings of the National Academy of Sciences. It's the seventh time in less than nine years that research from Zeng's lab has been published in one of the three major international multidisciplinary journals (Nature, Science and PNAS).

"That idea by Angell was realized by Jaeil in the computer simulation," said Zeng, Ameritas university professor of chemistry. "It's a very flat, single-layer ice clathrate. We call it a 'square-octagon ice clathrate' and we may nickname it 'Nebraska ice clathrate' because it's very flat."

As the two-dimensional ice formed under negative pressure, it developed into an interlocking pattern of small square-shaped openings and larger octagonal-shaped openings similar to the wallpaper pattern called Archimedean four-eight tiling. Hydrophobic argon atoms used in the experiment filled the octagonal "cages" in the ice clathrate [movie] [image].

Bai next tried the experiment without the argon atoms, again under negative pressure, in a hydrophobic slit pore about 0.6 nanometers wide (a nanometer is 1 billionth of a meter). He wanted to see if he could form the ice alone, without the argon as a "guest." The result was the discovery of a "guest-free" monolayer ice that forms spontaneously and remains stable [movie]. Zeng said his friend, professor E.G. Wang, dean of physical sciences at Beijing University, found the same pattern in 2004, but needed a silica template. "We were able to see for the first time a spontaneous formation of this ice," Zeng said.

A third discovery from the experiment was the coexistence of low- and high-density, two-dimensional ices. The low-density ice behaves like Ice I, the everyday kind of ice we find in our ice-cube trays at home. Just like regular ice, if the low-density, two-dimensional ice is subjected to increased pressure, it becomes liquid. Under even more pressure, it becomes the high-density ice, thus going from solid to liquid to solid. Putting almost any other solid under higher pressure forms only a denser solid.

"Ultimately, we want to understand the formation of three-dimensional ice clathrates on the molecular scale," Zeng said. "That could help scientists and engineers learn how to tap into the vast methane hydrates mostly trapped under the ocean floor."

Zeng said the Department of Energy estimates that the methane clathrates could provide some 20,000 terawatt-years of energy, compared to the 1,000 terawatt-years estimated to remain in conventional oil and gas. As a point of reference, global energy use in 2008 was about 15 terawatt-years. In addition, the undersea ice clathrates could be a site to store carbon dioxide, reducing the threat of global warming.

The research was conducted through the University of Nebraska's Holland Computing Center and supported by funding from the Department of Energy and the Nebraska Research Initiative.

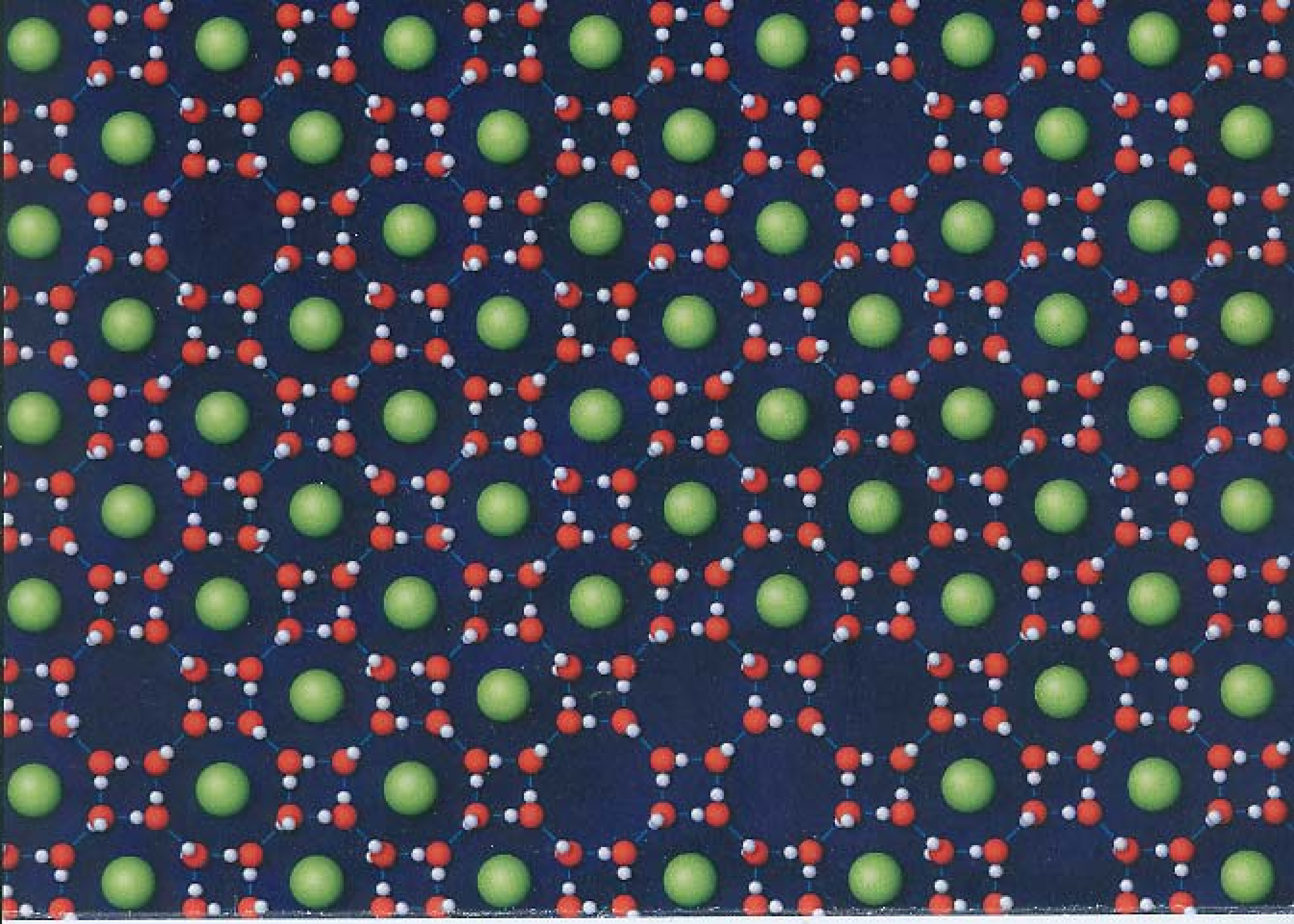
WRITER: Tom Simons, University Communications, (402) 472-8514

News Release Contacts:

- Xiao Cheng Zeng, Professor, Chemistry
  phone: 4024729894

Associated Media Files:

- Xiao Cheng Zeng (left) and Jaeil Bai
- Square-octagon ice clathrate with argon atoms (green) inside octagonal openings
- Computer-generated movie of formation of square-octagon ice clathrate (argon in green)
- Computer-generated movie of formation of guest-free monolayer ice (no argon)



Cover image: Square-octagon ice clathrate with argon atoms (green) inside octagonal openings. This image was created from a simulation of two-dimensional ice crystals formed under extreme conditions.

University of Nebraska-Lincoln Chemistry professor Xiao Cheng Zeng and his research associate, Dr. Jaeil Bai, discovered that ice molecules confined under severe conditions (~5000 atm, -10°F) can form cages that can trap other molecules. This research is aimed at understanding, on the molecular level, how methane is trapped in undersea ice; this understanding could help researchers devise methods for tapping suboceanic methane, which could become a crucial energy source for the future.

IDeA
EPSCoR
NEBRASKA