

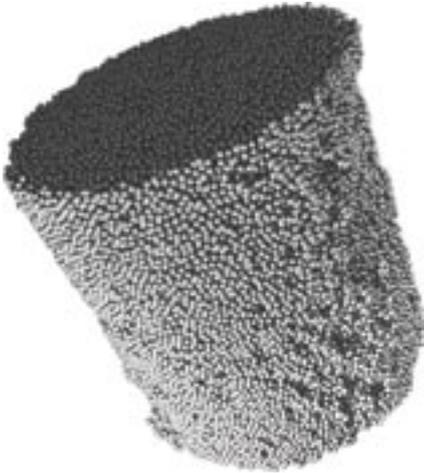
# CSEM's Materials Monthly

July 2005

Making materials matter

## New explorations in disorder

### The case of the packing spheres



Research at ANU is demonstrating that there is no pattern in the manner in which balls pack down. However, while the balls may be disordered they are not random. What's more, this disorder in some situations can be the most efficient way to be.

Filling containers with balls is an occupation that has fascinated humans of all ages since the beginning of recorded history. Seeking out a pattern in a stack of spheres sounds like child's play yet attempting to describe it mathematically has proved fiendishly difficult. Physicists at ANU are now throwing new light on the topic of packing spheres, and their insights promise to revolutionise our understanding of irregular structure in materials.

It's long been believed that when spheres pack down together that there is no discernable pattern or order in their arrangement but proving it mathematically has been very difficult.

#### Dealing with disorder

"Order is relatively easy to describe," says Dr Tomaso Aste from the Department of Applied Maths (RSPHysSE). "It doesn't require a lot of information to describe a crystalline structure, once you know the basic local symmetry and the translational rules you can reconstruct the whole structure. Order is convenient, and in many cases it's a very efficient way to go.

"Disorder, however, is neither easy or convenient to deal with and I think that because of this we tend to avoid engaging with it. Neither our language nor our maths are effective at describing disorder

and it's usually done by referencing it back to ordered systems.

"Indeed, even the name 'disorder' means 'absence of order'.

"The irony is that we consider the world to be an ordered place when in actual fact disorder is everywhere. Indeed, in Nature order is more the exception than the rule. This is particularly the case when you consider complex structures such as polymers, glasses or biological systems."

Dr Aste studies complex materials and his focus is on granular matter, foams and packings. Indeed, he's internationally renowned for his work on sphere packings, and an author of one of the few general books on the topic (titled *The pursuit of perfect packing*).

"Like most materials scientists, my training in physics was based on understanding highly ordered materials like crystals," explains Dr Aste.

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Dr Tomaso Aste with a container of the tiny acrylic balls he used in his landmark study.



# ANU

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# Dealing with disorder

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"However, it became apparent to me that understanding disorder was more important in terms of understanding the structure of materials and this inevitably led to the challenge of understanding the packing of spheres."

## Mapping balls

To study the structure of a large number of spheres that have settled in a container is very difficult as, in absence of a general theory, we need information about the exact position, orientation, shape and connectivity of each element. In the past this has been an extremely laborious process.

One of the landmark studies in this area, for example, was done back in the early 60s. It involved filling a container with 1000 small steel spheres and embedding this stack in wax. The structure of this pack was then analysed by making thin sections through the stack and physically measuring the position of each sphere in relation to every other sphere. Beside taking an enormous amount of time to collect the data, processing that data set was beyond the computer power available at that time.

## Packing numbers

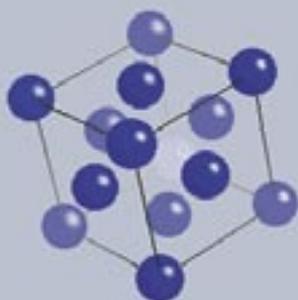
When it comes to random packing spheres the name of the game is the packing fraction, or how much of the available space the balls occupy. The best you can make is 0.74 (ie 74% balls, 26% space between the balls) as predicted by the Kepler's conjecture. However, in any practical situation the structure is disordered and the best you can hope to achieve is 0.64.

Though, if you're simply dropping the balls into the container you're more likely to achieve something around 61%. Shake the container holding the balls and the packing fraction increases to 63%. Shake the container and compact the mass of balls at the same time and you may achieve the target of 64%.

## Kepler's conjecture

Efficiency in packing spheres has preoccupied humans for a long time. How do you fit the most balls in the least space. It might be grapefruit in a fruit stall or cannon balls in a ship hold. Towards the end of the 16th Century a British mathematician named Thomas Harriot posed the question: what arrangement of balls takes up the least space? He wrote to his colleague Johannes Kepler, the famous astronomer, who experimented with different arrangements and concluded that an arrangement known as face-centred cubic packing (pictured below), a pattern favoured by fruit sellers since time immemorial, could not be bettered. In this arrangement there is a ball at each corner of the cube and one on each face. The volume taken up by the highly ordered spheres is 74% of the available volume.

This then became the Kepler Conjecture. While it's easy to demonstrate, proving it mathematically has taken centuries and required the advent of advanced computers.



"Studies on disorder and the packing of spheres are not easy," says Dr Aste. "In many ways it's taken the advent of computers and advanced materials technology to allow us to truly get a handle on it."

One of the reasons Dr Aste joined the Department of Applied Maths was because of the facilities and expertise that are available there to pursue studies on disorder.

"The theoretical, experimental and numerical capacities in Applied Maths makes it a truly unique environment for work on disordered systems," he says. "This has allowed us to carry out a study on the largest empirical data set on packing

spheres that has ever been recorded."

## The biggest data set

The team lead by Dr Aste measured the positions of more than 385,000 1mm acrylic spheres in 6 different packings. The measurements were made with the Department's Computer Tomography X-ray facility. Tomography involves X-ray imaging slices of the sample and then using a computer to put these slices together to build a 3D model of its structure. Then it was a matter of using the awesome computational power of the ANU Supercomputer Facility to work with the data set.

"We searched this data for signatures of organisation, looked for local configurations, their relative occurrences, their correlations, and the resulting hierarchical structure," says Dr Aste. "And the resounding message coming out of our results is that the system is truly disordered but it is not random. It is highly organised with correlations which go far beyond first neighboring spheres.

"Our analysis also showed us that these disordered

arrangements can yield amorphous packings which are actually more efficient than crystalline aggregates in some situations.

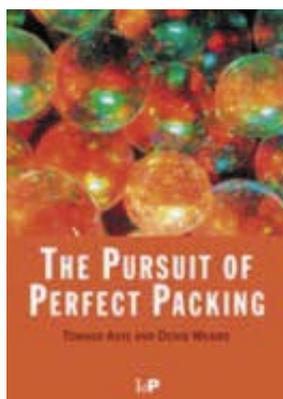
“While these findings sound somewhat academic they have important implications for our understanding in many small-scaled systems where little numbers of atoms in nano-sized clusters are involved. In such systems disordered configurations can have relatively large packing fractions, large particle interconnectivity and small surface-to-volume ratio. This has significant consequences for our work on a range of nano-materials.”

### Granular materials

Understanding the disordered nature of packing spheres also has applications in the way we work with day to day granular materials.

“Granular materials are ubiquitous in nature and in human activity,” explains Dr Aste. “They include cereal grains, powders, sand and coal. The worldwide annual production of cereals and aggregates of various kinds is gigantic, reaching approximately 10 billion tonnes each year. Coal, for example, accounts for about 3.5 billion tonnes, while cement, and gravel for construction account for 2 billion.

“The processing of these materials consumes roughly 20% of the energy produced on this planet. Estimates suggest we waste 40% of the capacity of many industrial plants because



Dr Aste's book on the packaging of spheres.

of problems encountered in dealing with these materials.

“These are staggering numbers but it might be that the very intractable nature of disordered materials has meant that in the past we've simply accepted that there's nothing we could do to improve the way we work with these materials. But that is now changing. Studies such as ours are making it possible to meaningfully describe and work with them.

“The flow on in applications should have strong scientific, technological and economical impacts in a wide range of fields from storing grain through to building new nano-materials.”

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A model of a pack of spheres generated through X-ray computer tomography. The different colours indicate the topological distance (number of links in the contact network) from a central sphere.



### Ideal disorder

Dr Zbigniew Stachurski is a materials researcher in the Department of Engineering, FEIT. He has had a long career studying amorphous polymers and glassy materials where the structure is disordered rather than ordered. Traditionally, such materials are understood by comparing them against corresponding ideal crystalline solids but in recent years Dr Stachurski has begun to believe this is the wrong approach.

“Rather than consider an amorphous solid as being at the limit of disorder of the corresponding crystalline solid, we need to turn things around,” says Dr Stachurski. “Because amorphous solids have their own set of rules we need to define an ideal amorphous solid first and then reference our real amorphous materials against this ideal.”

Towards this end Dr Stachurski has formulated an elementary model of an ideal amorphous mono-atomic solid. The model regards clusters of touching spheres as being the building blocks of amorphous solids. The solid can then be described by two statistical functions.

Using this ideal model, structural imperfections in the amorphous structure, called ‘flaws’, can now be defined. Some flaws increase the density of the ideal amorphous solid, whereas other flaws decrease its density. This is quite different to crystalline materials where defects always decrease density.

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A cluster of spheres with a random configuration.

# More than a hairy scratch

The letters A, N and U pictured below right are each just under a millimetre in width. That's small but not particularly noteworthy. However, when you ramp up the magnification a couple of orders of magnitude the magic of the letters starts to become apparent because these letters are actually composed of millions of nanoscale hairs or tubes growing out from scratches on the surface of a silicon wafer. Indeed this is a patterned growth of carbon nanotubes on silicon and it's a world first for Dr Ying Chen and his team in the Department of Electronic Materials Engineering (RSPSE).

"Growing large quantities of carbon nanotubes on predesigned patterns and at desired locations on different substrates is an important part of integrating nanotubes into nanoscale devices and sensors at a commercial scale," says Chen. "While there's been some success growing nanotubes on silicon dioxide substrates primed with metal catalysts using chemical vapour deposition, it hasn't been achieved on pure silicon substrates."

Ying Chen's team achieved the feat using the ball milling technique that Chen has developed in recent years. Ball milling involves grinding the precursor materials that will make the nanotubes into an ultra-fine powder in a revolving chamber full of ball bearings. In this case, a couple of grams of iron phthalocyanine (a material that contains both the carbon source and the metal catalyst required for carbon nanotube growth) is ground up in a ball mill for 100 hours (at room temperature in argon gas at a pressure of 300kPa). The argon prevents oxidation during the milling process.

The milled sample is then placed in a quartz furnace next to a silicon wafer with a pattern scratched onto it using a diamond pen (in this case the letters A, N and U). The milled powder is then heated converting it into a vapour which is then carried in a stream of argon to be deposited on the

wafer. Further heating results in carbon nanotubes growing from the scratched portions of the silicon wafer but no where else on the wafer.

When examined with a transmission electron microscope the nanotubes were shown to be multi-walled cylinders measuring some 50 nanometres in diameter.

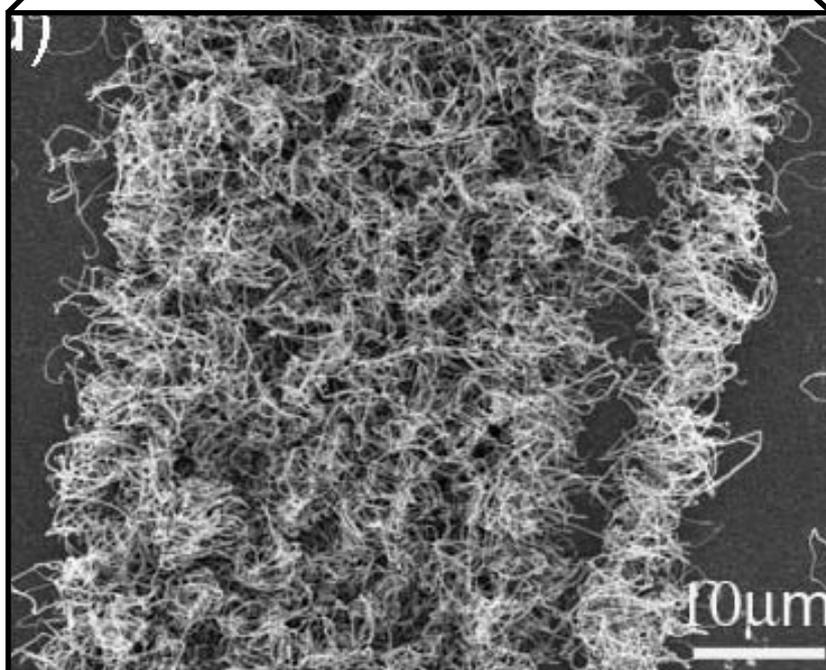
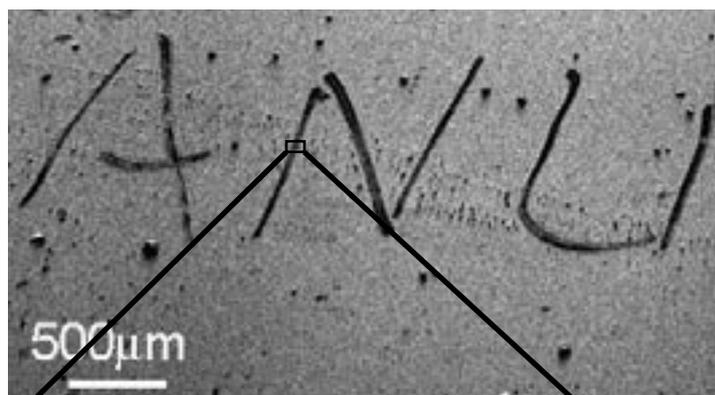
"The selective growth of the carbon nanotubes over the scratched surface on the silicon substrate is a typical self-assembly process possibly driven by capillary force," says Chen. "The successful selective growth on complicated patterns such as the three letters of A, N and U is an important step towards building nanotube devices."



Dr Ying Chen

Their technique for growing patterned carbon nanotubes on silicon substrates has been published in the July issue of Applied Physics Letters, 87, 1 (2005).

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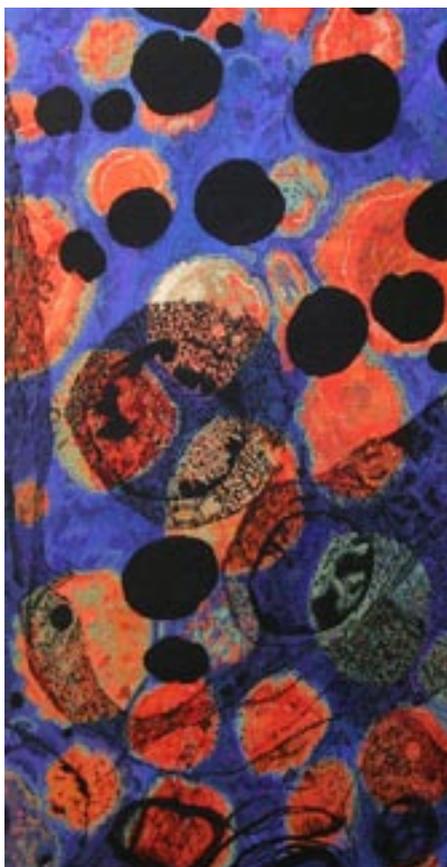
# The full picture

In the May issue of *Materials Monthly* we showed you the beginning of a tapestry being created by Valerie Kirk to celebrate Professor Peter Doherty and Professor Rolf Zinkernagel for their Nobel-winning research on cell mediated immune response. Below is the completed tapestry. Measuring 1.2 m wide by 2.4 m deep, the tapestry will soon be adorning the walls of University House.

The Doherty/Zinkernagel tapestry is one of three tapestries being created by Ms Kirk as part of celebrations of the 50th birthday of University House. The theme of the series is Nobel laureates at ANU and the other two tapestries reflect on the research of Sir John Eccles (ionic mechanisms of the nerve cell) and Lord Howard Florey (penicillium and antibiotics).

The Eccles tapestry has also been completed and Valerie is now busy at work at the Florey tapestry. The Nobel tapestries should be complete and on display before years end.

**MM**



## Order, disorder & criticality

Last month CSEM ran a highly successful symposium on order and disorder in materials. Speakers came from all over ANU as well as from the University of Sydney, University of NSW, CSIRO and the Royal Melbourne Institute of Technology. Presentations covered a diverse range of topics including disordered sphere packings (see feature story), glassy systems, complex crystal structures, supercooled liquids and amorphous alloys. Held in the Forestry Building (pictured above), the symposium was an excellent opportunity for researchers in this rapidly emerging field to network.

**MM**

## Tiina's last coffee

CSEM says a fond farewell to Tiina Hatherall, our office administrator for the last one and half years. Tiina would be familiar to anyone who has attended any CSEM or Future Materials event over the last year. Besides taking bookings, arranging venues and managing the mailout of *Materials Monthly*, Tiina invariably oversaw the catering of events and you may have met her serving coffee or offering dessert. Tiina's last coffee, however, was served to her instead when CSEM took her out for a farewell lunch.

Tiina also put considerable time into building up the Future Materials Research Capabilities and Expertises Database. She is moving to Brisbane but we hope to remain in contact because she will be doing some more work building up the Database for the Brisbane office of Future Materials at the University of Queensland.

**MM**

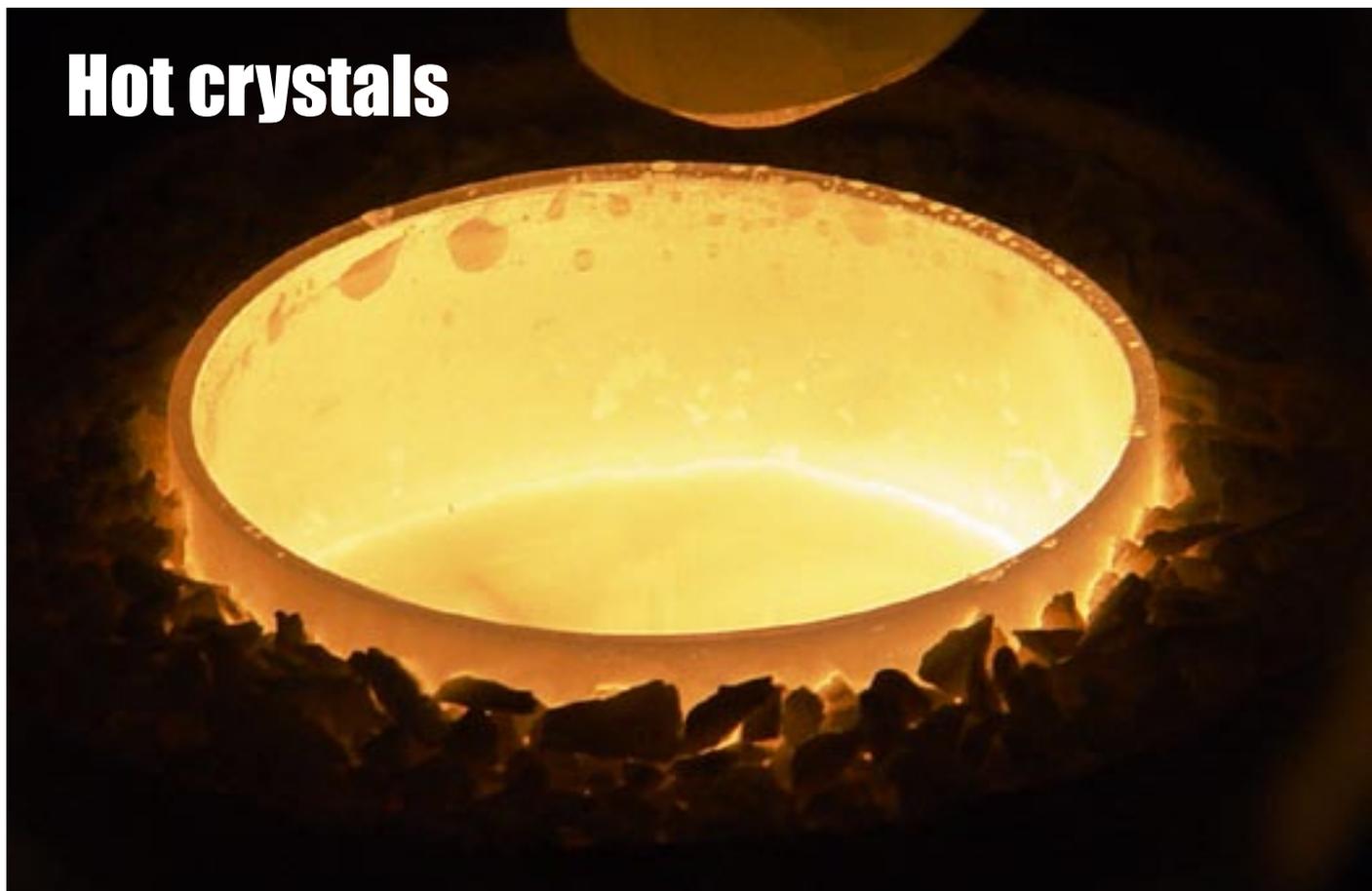


(above) Tiina serves lunch at the 'Materials @ ANU' forum last year.

(right) CSEM and Future Materials say farewell to Tiina. From the left, Tiina, David Salt, Zbigniew Stachurski and Ulrich Theden.



# Hot crystals



by Anita Smith

Pictured above is an inductively heated iridium crucible being used to grow a single crystal of yttrium orthosilicate. The crucible is heated to temperatures in excess of 2000°C. It's part of the Crystal Growth Facility at the Laser Physics Centre (Research School of Physical Sciences and Engineering).

This method of growing crystals is known as the Czochralski technique. It is the most widely utilised method for the growth of high-grade optical quality crystals of materials with high melting points.

Induction heating has many advantages over other heating methods. High temperatures are easily achievable and can be reached in relatively short periods of time. Induction heating also allows the temperature of the molten crystal solution to be precisely controlled, resulting in greater melt stability and higher quality crystals. These capacities mean that a variety of novel and specialised high temperature materials can be produced for a wide range of applications.

A major research effort within the Solid State Spectroscopy group at the Laser Physics Centre is the development of new high-resolution laser techniques for information

processing utilizing quantum coherence effects in crystals. The crystals required for this research are high optical quality transparent crystals doped with optically active rare-earth ions. The high temperature crystals produced by the Czochralski technique are perfect for these studies.

These crystals have applications in quantum information processing. Examples of these applications include:

1. Quantum computing;
2. Information storage;

3. Optical processing of radar signals.

Commercially significant applications of crystals grown using the Czochralski technique include solid state laser rods, such as Neodymium doped yttrium aluminium garnet, and electro-optic crystals such as lithium niobate.

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Photo by Tim Wetherell



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Please let us know if you wish to be added to our electronic or postal mailing lists.

Electronic copies of *Materials Monthly*, useful links and additional information about CSEM can be found at our website: [www.anu.edu.au/CSEM](http://www.anu.edu.au/CSEM)

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