MATERIALS SCIENCE

Viewing the Seeds of Crystallization

Electron microscopy is providing glimpses of the complex structural processes that precede crystal nucleation.

J. Murray Gibson

All materials search for the lowest accessible energy state. As temperature is increased in disordered materials, atoms diffuse and explore different chemical and structural configurations. Crystalline phases may be favored, but a very small crystal is unstable, so there is a "nucleation barrier" to overcome; only after reaching a critical size can the nucleus grow. Although we understand the thermodynamics of the nucleation process [e.g., (*1*)], observation of the actual atomic-scale complexity during nucleation has remained elusive, despite its importance to the properties of materials. Taking nucleation out of the "black box" is one of the grand challenges to "materials by design" that is seen as the future solution to major societal problems such as sustainable energy (*2*). On page 980 of this issue, Lee *et al*. (*3*) use fluctuation electron microscopy to image subcritical nuclei in a solid material, observing metastable structural states that facilitate later nucleation in amorphous films. Their study is applied to a technologically important case of "phase-change memory" and therefore may facilitate efforts to design faster higher-density nonvolatile memory.

Nucleation is ubiquitous. It determines when a menacing cloud will start to pour out rain, or when a pan on the stove will boil. Suppressing ice nucleation helps fish live in ice-cold water (*4*). Nucleation of amyloid fibers is suspected to be critical to the development of neurodegenerative diseases (*5*). Nucleation of crystalline ice is dependent on impurities and other conditions, and this has been used to produce beautiful ice "paintings" (*6*) (see the figure). The nucleation of crystals in amorphous materials or liquids, as studied by Lee *et al*., is often a determining step in the processing of materials. Crystal nucleation is responsible for the write cycle in a DVD, but it is also key to steel production, manufacturing of solar cells, and the production of food.

Although very small crystalline nuclei have been observed on exposed crystal surfaces (*7*), reports of subcritical nucleation observation in bulk materials are scarce (*8*). The scale and density of crystal nucleation sites inside liquids or disordered materials is usually very small, typically on the atomic scale, which makes them very difficult to probe. It is hard to distinguish crystalline structure from disorder when the correlation length of the crystals is just a few atomic spacings. Fluctuation microscopy was developed to address this problem (*9*, *10*).

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA. E-mail: jmgibson@aps.anl.gov

Ice paintings. Exploiting the complexity of ice crystal nucleation to produce beautiful art (*6*). Nucleation is controlled through cooling rates and impurities, which also lend color to the ice.

CREDITS: GORDON HALLORAN/WWW.ICEPAINTINGPROJECT.COM. PHOTO: ALLAN BURNS

Scattering techniques with diffracting radiation such as x-rays, neutrons, and electrons tell us most of what we know about the atomic configurations in solids. Yet averaging techniques are not well suited for detecting nucleation that begins with vanishing volume fraction. Today, fast electrons are unique in their subsurface sensitivity and spatial resolution, permitting diffraction from highly localized nanoscale volumes, and thus could detect nucleation. The difficulty in doing so, however, is that crystal nucleation often occurs in highly disordered or amorphous matrices. In this case we have to contend with the quasi-random scattering fluctuations ("speckle") that arise from nanoscale volumes. Fluctuation microscopy focuses on statistical analysis of fluctuations to overcome the limitations of visual inspection. It can reveal prototypical crystalline order through sensitivity to higher-order atomic correlations that pick out crystalline topology (*9*). The first experimental use showed that amorphous elemental semiconductors contain more crystalline topological order than expected from a random network model, and that upon gentle annealing the order dissolves (*11*). Since then there have been growing applications to other amorphous materials (*10*).

"Phase-change" materials (*12*) are now widely used in optical and electronic memories (*13*). Certain chalcogenide amorphous semiconductors exhibit a change in reflectivity (and electrical resistivity) between crystal and amorphous phases and can be rapidly and reversibly switched between the two states by heating. Slower heating yields the crystalline phase, whereas fast heating and cooling leaves the amorphous phase. A recent use of these materials is in solid-state circuits for nonvolatile high-speed, high-density memory, where thermal switching uses resistive heating and the change in resistivity between states is exploited as a memory. Key to the application is control of crystal nucleation during switching, and the stochastic nature of this limits the speed and density of the memory. There are many handles to turn in the material's stoichiometry and processing that can affect nucleation, but the results to date have been mostly empirical. A better understanding of nucleation will lead to new approaches to control and improve the process. Lee *et al*. show that preannealing favors faster nucleation because it leaves subcritical seeds in the material.

We expect to see further application of techniques that probe higher-order correlations as a tool to understand nucleation and structure in disordered and partially crystalline substances. Beyond fluctuation microscopy, there are related approaches that also look promising (*14*). Revolutions in focusing and brightness make related techniques accessible with penetrating x-rays. Fluctuation microscopy is a fingerprint technique. It is sensitive enough to allow one to distinguish models, but it is difficult to directly interpret data. Further advances will occur by combining fluctuation microscopy data and other structural data in Monte Carlo structural refinements. Progress is needed in the theory underlying interpretation, with the ultimate goal that high-order correlation functions can be directly determined without modeling (*15*). Such developments will provide a better fundamental understanding of amorphous materials and crystal nucleation, resulting in better phase-change memory and other technologies.

References and Notes

1. D. Kaschiev, *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000).
2. U.S. Department of Energy Basic Sciences Advisory Committee, *New Science for a Secure and Sustainable Energy Future* (2008) (www.sc.doe.gov/bes/reports/files/NSSSEF_rpt.pdf).
3. B.-S. Lee *et al.*, *Science* **326**, 980 (2009).
4. I. Peterson, *Sci. News* **130**, 330 (1986).
5. J. T. Jarrett, P. T. Lansbury, *Cell* **73**, 1055 (1993).
6. The artwork of Gordon Halloran (see, for example, www.icepaintingproject.com).
7. D. E. Jesson, M. Kastner, B. Voightlander, *Phys. Rev. Lett.* **84**, 330 (2000).
8. K. F. Kelton *et al.*, *Phys. Rev. Lett.* **90**, 195504 (2003).
9. M. M. J. Treacy, J. M. Gibson, *Acta Crystallogr.* **A52**, 212 (1996).
10. M. M. J. Treacy *et al.*, *Rep. Prog. Phys.* **68**, 2899 (2005).
11. J. M. Gibson, M. M. J. Treacy, *Phys. Rev. Lett.* **78**, 1074 (1997).
12. S. Ovshinsky, *Phys. Rev. Lett.* **21**, 1450 (1968).
13. S. Raoux, *Annu. Rev. Mater. Res.* **39**, 25 (2009).
14. P. Wolchner *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 11611 (2009).
15. T. Iwai *et al.*, *Phys. Rev. B* **60**, 191 (1999).

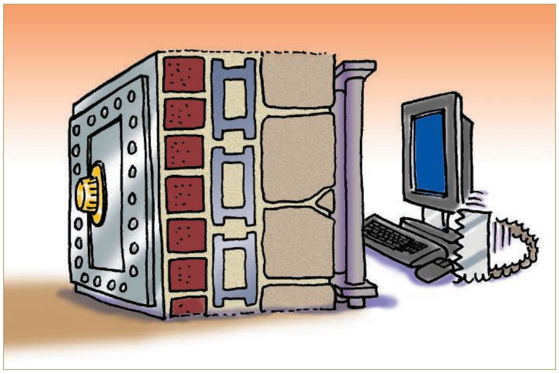
10.1126/science.1182817

COMPUTER SCIENCE

Reflections on Cybersecurity

The lack of security in cyberspace may be addressed by learning from the strengths of the Internet.

William A. Wulf and Anita K. Jones



CREDIT: JOE SUTLIFF/WWW.CDAD.COM/JOE

> Perfection is achieved, not when there is nothing more to add, but when there is nothing left to take away.
>
> –Antoine de Saint-Exupéry in *The Little Prince*

Cyberspace is less secure than it was 40 years ago. That is not to say that no progress has been made—cryptography is much better, for example. But more vital information is accessible on networked computers, and the consequences of intrusion can therefore be much higher. A fresh approach is needed if the situation is to improve materially.

The prevailing assumption continues to be that if systems were implemented correctly, the problem would be solved. Yet, software engineers have tried to do that for 40 years and have failed. A 1993 report from the Naval Research Laboratory (*1*) points to a deeper problem. It analyzed some 50 security breaches, and found that in 22 of those cases, the code correctly implemented the specifications—it was the specifications that were wrong. They handled the usual cases just fine, but did not appreciate that under some circumstances, permitted actions or outcomes were, in fact, security breaches.

A natural tendency is to declare a crisis and convene task forces and an army of programmers to "fix" the security problem(s). But, as detailed in Fred Brooks' *The Mythical Man-Month* (*2*), trying to get more "man months per calendar month" can actually make the situation worse, not better. We conjecture that a similar phenomenon is occurring for cybersecurity. The security model has remained the same since the 1960s, and software engineers have added more and more patches and widgets to try to enforce that security model. The complex interaction of this additional code with the extant code just provides more opportunities for security failures. The cybersecurity community must thus ask whether the problem has been formulated in the right way.

The current model for most cybersecurity is "perimeter defense": The "good stuff" is on the "inside," the attacker is on the "outside," and the job of the security system is to keep the attacker out. The perimeter defense model is built deeply into the very language used to discuss security: Hackers try to "break in," "firewalls" protect the system, "intrusion" must be detected, etc. But is perimeter defense the right underlying model?

We do not think so, for several reasons. First, perimeter defense does not protect against the compromised insider. The Federal Bureau of Investigation (FBI) has reported that in one sample of financial systems intrusions, attacks by insiders were twice as likely as ones from outsiders—and the cost of an intrusion by an insider was 30 times as great (*3*).

Second, it is fragile; once the perimeter has been breached, the attacker has free access. Some will say that this is why "defense in depth" is needed—but if each layer is just another perimeter defense, all layers will have the same problems.

Third, and most important, it has never worked. It did not work for ancient walled cities or for the French in World War II (at 20 to 25 km deep, the Maginot Line was the most formidable military defense ever built, yet France was overrun in 35 days). And it has not worked for cybersecurity. To our knowledge no one has ever built a secure, nontrivial computer system based on this model.

So, what might be an alternative approach? We think we should take our cue from the Internet. That is, there should not be just one model. Rather, there should be a minimal central mechanism that enables implementation of many security policies in application code—systems attuned to the needs of differing applications and organizations.

It is worth noting that the Internet succeeded so well precisely because it does so little. At its core, the TCP/IP protocols, all the Internet does is to promise "best effort" message delivery. It does not promise that the messages will arrive in the order in which they were sent, that they will ever arrive at all, or even that the same message will not

Department of Computer Science, University of Virginia, Charlottesville, VA 22903, USA. E-mail: wulf@virginia.edu, jones@virginia.edu

Published by AAAS