CONDENSED MATTER PHYSICS

Catching structural transitions in liquids

Femtosecond pulse x-ray diffraction reveals structural changes between liquid states

By Feng Rao[1], Wei Zhang[2], Evan Ma[3]

Phase-change random-access memory is a key ingredient for nonvolatile memory and neuro-inspired computing devices (*1*, *2*). It exploits the ability of chalcogenide phase-change materials (PCMs) to rapidly switch between logic states "0" (glassy) and "1" (crystalline). The "0" state is reached through fast quenching of the melted PCM (cooling at a rate that retains the amorphous atomic arrangement in the liquiid). In this process, the diffusivity and viscosity change by ~17 orders of magnitude, the majority of which happens over a narrow temperature range (*1*). What is happening inside the cooling liquid to make this possible has remained elusive because characterization that requires nanoseconds of measurement time is intercepted by crystallization. On page 1062 of this issue, Zalden *et al.* (*3*) overcame this challenge by using femtosecond pulse x-ray diffraction and captured a liquid-liquid transition (LLT) in PCM liquids during superfast cooling.

The finding of Zalden *et al.* has implications for better understanding PCM-based device operation. Although the "0" state allows data storage for a very long time at room temperature (300 K), it only takes nanoseconds to transform into the "1" state, when the glassy solid is heated to above its glass transition temperature (T_g) (for example, up to 700 K). This echoes the drastic jump in the dynamics of the supercooled liquid PCM over a narrow temperature window. A plausible explanation is that there is a LLT with an underlying structural transformation.

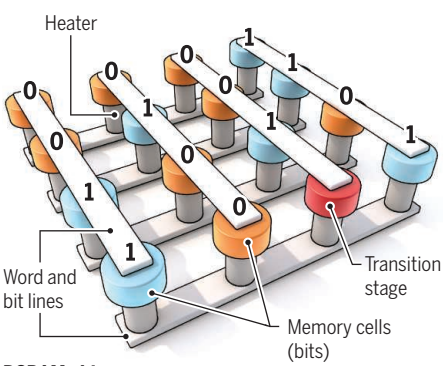
Zalden *et al.* used laser pulses (each 50 fs in duration) to heat a thin film of a PCM [either AgIn-doped Sb_2Te (AIST) or $Ge_{15}Sb_{85}$] above its melting temperature (T_m) and then monitored the atomic structure with femtosecond x-ray diffraction as the PCM was undergoing rapid quenching to avoid crystallization. The short time interval of the x-ray pulses ensured accurate tracking of atomic structure with minimal atomic motion. The radii ratio ($R = r_2/r_1$) of the first and second coordination shells [which refers to a central atom and the nearest atoms around it (first shell) and second nearest neighbors (second shell)] increased as the liquid quenched, displaying an inflection point in the slope of the R curve at ~660 and ~610 K for AIST and $Ge_{15}Sb_{85}$, respectively, which is well below the T_m of each PCM. The inflection point is referred to as T_{LL}, the temperature of a LLT. This structural transformation was attributed to oscillations in bond length known as Peierls distortion. This results in long and short bonds, starting from an octahedral-like atomic environment (see the figure). Zalden *et al.* noted a pre-peak in the x-ray scattering spectra when approaching T_{LL}, indicating periodic correlations in real space at ~6.0 Å. This corresponds to twice the typical bond length (~3.0 Å) in AIST and $Ge_{15}Sb_{85}$. Such periodic characteristics are consistent with long-short bonding pairs having an ~180° bonding angle. First-principles molecular dynamics simulations indicate that a pseudo–band gap opens up that accompanies the increasing Peierls distortion as electrons become more localized between atoms. Zalden *et al.* associate their observed pronounced increase in Peierls distortion to a LLT, akin to the case in phosphorous in which polymerization causes a LLT with changes in electronic properties (*4*).

For AIST, ultrafast differential scanning calorimetry (*5*) and laser-reflectivity measurements (*6*) suggested a fragile-to-strong liquid transition during cooling. For a "strong" liquid (such as silica), its viscosity follows Arrhenius behavior, with a nearly constant activation energy for viscous flow from the T_g to T_m. For a "fragile" liquid (such as o-terphenyl), the apparent activation energy is rather high (near the T_g) but decreases as the temperature increases (*7*). A fragile-to-strong liquid crossover could explain the high atomic mobility at elevated temperatures for fast crystallization and yet sluggish diffusion at room temperature for long-term data retention. Zalden *et al.* explicitly associated the LLT implicated by Peierls distortion with the fragile-to-strong liquid crossover.

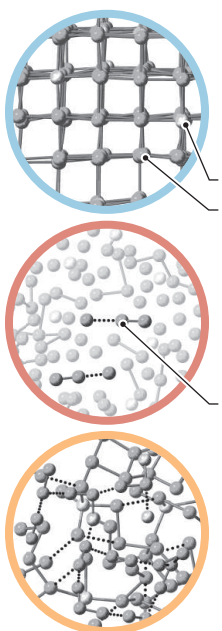
Challenging issues remain with regard to Peierls distortion as the sole structural origin of the fragile-to-strong liquid crossover. Although the LLT identified is expected to render an increment in the energy barrier for viscous flow, the actual escalation in activation energy should be assessed to compare with the known data (*5*, *6*). Also, it seems possible that Peierls distortion can appear at a temperature much higher than the temperature window found for fragile-to-strong

Phase-change memory

A memory device can use a phase-change material (such as $Ge_{15}Sb_{85}$) to switch quickly between logic states "1" (crystalline) and "0" (amorphous). These states are programmed through reversible phase transformation.



PCRAM chip
Memory cells (blue, orange) made of phase-change material are arranged in a crossbar phase-change random access memory (PCRAM) array.



GRAPHIC: C. BICKEL/*SCIENCE*

[1]*College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China.* [2]*Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China.* [3]*Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, USA. E-mail: fengrao@szu.edu.cn; wzhang0@mail.xjtu.edu.cn; ema@jhu.edu*

crossover (*5*, *6*). If the amplitude of Peierls distortion increases gradually, there could be additional structural mechanisms that set off the much sharper rise of the apparent activation energy of viscosity-diffusivity at the "knee" observed in the Angell plot of some PCMs (*5*, *8*). For example, there could be structural heterogeneities at or beyond medium range that cause dynamical heterogeneities resembling glass-like behavior. The role of more flexible long bonds, and the possible cross-linking organization into an extended network, should be examined. First-principles molecular dynamics simulations have shown an *R* parameter less temperature dependent than the experimental finding. One possible reason is the rapid cooling rate and the inadequate equilibration time at each temperature step in simulations. This discrepancy is compounded by a lack of atomistics data on the unconventional dynamics in supercooled PCM liquids. An in-depth understanding may become manageable by using the interatomic potentials developed with machine-learning methods (*9*).

Femtosecond x-ray diffraction and absorption spectroscopies can be used to probe into liquid states in the already commercialized $Ge_2Sb_2Te_5$ (*8*) and the recently designed $Sc_{0.2}Sb_2Te_3$ (*2*) PCMs, in which nucleation, rather than growth (as in AIST and $Ge_{15}Sb_{85}$), plays a dominant role for nanoseconds operation. In general, LLTs appear to occur often, in systems from water to PCMs to metallic glass–forming liquids (*10*). However, LLTs are difficult to confirm experimentally—not to mention the lack of a systematic understanding as to which material systems exhibit them, and when, and why. In all cases, LLTs should feature a clear structural indicator. The approach of Zalden *et al.* opens a new avenue for interrogating the complex and swift structural changes in highly dynamic liquids. This should ultimately aid in optimizing the performance of PCM-based devices. ■

REFERENCES AND NOTES

1. W. Zhang *et al.*, *Nat. Rev. Mater.* **4**, 150 (2019).
2. F. Rao *et al.*, *Science* **358**, 1423 (2017).
3. P. Zalden *et al.*, *Science* **364**, 1062 (2019).
4. Y. Katayama, *J. Non-Cryst. Solids* **312-314**, 8 (2002).
5. J. Orava *et al.*, *Adv. Funct. Mater.* **25**, 4851 (2015).
6. M. Salinga *et al.*, *Nat. Commun.* **4**, 2371 (2013).
7. S. Wei *et al.*, *Acta Mater.* **129**, 259 (2017).
8. J. Orava *et al.*, *Nat. Mater.* **11**, 279 (2012).
9. F. C. Mocanu *et al.*, *J. Phys. Chem. B* **122**, 8998 (2018).
10. C. P. Royall, S. R. Williams, *Phys. Rep.* **560**, 1 (2015).

ACKNOWLEDGMENTS

F.R. thanks the National Natural Science Foundation of China (61622408), the Major Provincial Basic Research Program of Guangdong (2017KZDXM070), and the Science and Technology Foundation of Shenzhen (JCYJ20180507182248605, JCYJ20170302150053136). W. Z. thanks the National Natural Science Foundation of China (61774123). E. M. is supported at Johns Hopkins University by the U.S. Department of Energy, Basic Energy Sciences, Division of Materials Science and Engineering, under grant DE-FG02-16ER46056.

10.1126/science.aax6333

GRAPHIC: N. DESAI/*SCIENCE*

MEMBRANES

Scaling up nanoporous graphene membranes

Practical desalination membranes with nanoporous graphene will need new morphologies

By **Baoxia Mi**

Suitably engineered graphene-based materials could potentially be used to make water-separation membranes for applications such as desalination. Graphene-based materials with water-permeable pores can be made by creating either nanopores in graphene monolayers (see the figure, top) (*1*, *2*) or two-dimensional (2D) channels that form between nanosheets of graphene oxide (GO) (see the figure, middle) (*3*). Both approaches face challenges for scaling to practical membrane sizes on the meter scale. The former requires creating a high density of subnanometer pores (*4*) on a defect-free monolayer graphene sheet that has high out-of-plane mechanical strength (*5*), and materials meeting all these requirements have largely been limited to micrometer-scale lateral dimensions. On page 1057 of this issue, Yang *et al.* (*6*) report production of nanoporous graphene on the centimeter scale that can reject between 85 and 97% of the salt from saltwater.

The difference in difficulty of scaling up the two approaches can be best appreciated by noting that unlike the challenging procedures for nanoporous graphene synthesis, centimeter-scale stacked GO membranes were readily made for initial bench-scale studies. Synthesis methods for GO have existed for decades, and it can be mass-produced through chemical oxidization and ultrasonic exfoliation of graphite (*7*). Thus, GO has proven less complicated and more economical to scale up.

The hydroxyl, carboxyl, and epoxide functional groups on GO can be chemically modified to help control the size of the 2D channel (the interlayer spacing) and produce membranes with different separation capabilities (*3*, *8*). However, these functional groups also create the major problem with the stacked GO membrane—swelling in aqueous solutions (*9*)—which often results in low salt rejection (fraction of salt removed), typically in the range from 30 to 80%. Physical confinement—for example, with a polymer—can increase salt rejection to 97% (*10*). However, this strategy is feasible for centimeter-scale GO membranes, but may be more complicated to achieve in large-scale applications.

Unlike GO membranes, nanoporous monolayer graphene membranes are not inherently tolerant to defects. As the graphene membrane area increases, it becomes more prone to defects that can create openings

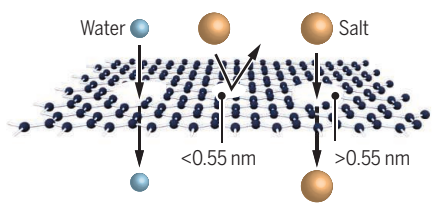
Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA. Email: mib@berkeley.edu

Toward practical graphene membranes

Combining two competing approaches may allow fabrication of meter-scale desalination membranes with two-dimensional materials.

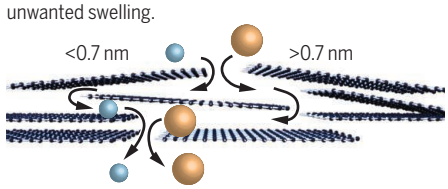
Through the pores

Salt molecules (both cations and anions) are rejected by nanopores in monolayer graphene that pass water. Yang *et al.* report centimeter-scale membranes of this type with low defect densities and high salt rejection.



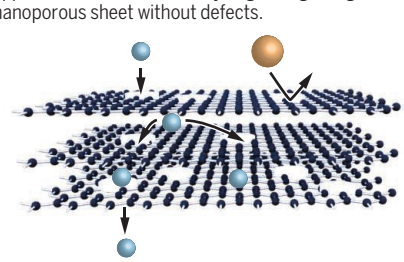
Around the stacks

In graphene oxide membranes, separation is achieved by water moving through channels between nanosheets faster than salt. Such membranes are prone to unwanted swelling.



Through and around

Meter-scale nanoporous graphene membranes could potentially be made by stacking smaller sheets. This approach avoids the difficulty of growing a large nanoporous sheet without defects.



Catching structural transitions in liquids

Feng Rao, Wei Zhang and Evan Ma

Science **364** (6445), 1032-1033.
DOI: 10.1126/science.aax6333