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September 29, 2014

The fragile-to-strong transition in metallic glass-forming liquids: How does it work? Liquids typically form glasses if they can be cooled without crystallizing. During the cooling process, a liquid's viscosity increases rapidly as it approaches its glass-transition temperature (T_g). If the rate of viscosity increase varies logarithmically with the drop in temperature (Arrhenius behavior), the liquid is said to be "strong", and the material has a broad T_g range. Otherwise, the liquid is "fragile", and has a narrower T_g range.

L. Hu and coauthors at Shandong University (Jinan, China), the Chinese Academy of Sciences (Beijing), Corning Inc. (Corning, NY), and Aalborg University (Denmark) studied a recently reported phenomenon, the fragile-to-strong (F-S) transition, by cooling and reheating ribbons of $\text{La}_{55}\text{Al}_{25}\text{Ni}_5\text{Cu}_{15}$ at various rates. They note that this transition is not observed in fragile liquids, but it occurs in many relatively strong glass-forming systems.

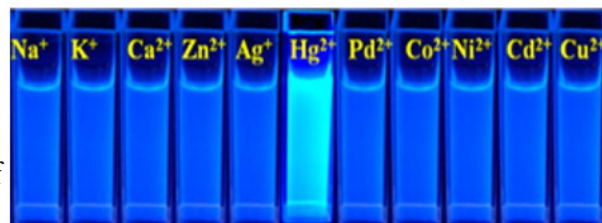
Previous studies examined the kinetic aspects of the F-S transition, but not much is known about its thermodynamic signature. The authors compared calorimetry scans for $\text{La}_{55}\text{Al}_{25}\text{Ni}_5\text{Cu}_{15}$ glass ribbons that were melt-spun (hyperquenched) and reheated (annealed) at various rates to characterize their crystallization behavior. The melt-spinning process cooled the ribbons rapidly, "freezing in" intermediate structures for examination. Reheating the ribbons at various rates in a differential scanning calorimeter (DSC) allowed the authors to monitor the heat flow characteristics as the ribbons annealed.

Glass ribbons spun at an intermediate rate (15–25 m/s) exhibited anomalous crystallization behavior when they were annealed, compared with glasses cooled at faster or slower rates. DSC traces for the anomalous samples split into a main peak and a shoulder, indicating the formation of more than one type of local structure, each with a different tendency to crystallize. This behavior implies the existence of a thermodynamic F-S transition. The authors believe that anomalous crystallization might be used as an indicator to detect and characterize the F-S transitions of other metallic glasses. (*J. Phys. Chem. B* DOI: 10.1021/jp504370y; Nancy McGuire)

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This molecule changes emission color when mercury is around. Mercury, in the form of Hg^{2+} , is a neurological toxin that is widely distributed in the environment by natural processes and human activities. Optical techniques for detecting mercury in the field and in living systems have the advantages of being simple, noninvasive, and sensitive. However, few existing fluorescence probes for Hg^{2+} are compatible with aqueous systems.



A. Misra and co-workers at Banaras Hindu University (Varanasi, India) designed and synthesized a simple molecular fluorescence probe that consists of a central anthracene molecule attached to two benzhydryl groups by piperazine bridges. This photoinduced electron transfer (PET) probe is highly selective for Hg^{2+} , and it can detect concentrations as low as 2 ppb, the US Environmental Protection Agency's "maximum tolerable level" in drinking water.

A positive response to Hg^{2+} is easily visible as the color of the probe changes from a fluorescent blue to blue-green. Other common cations do not cause this color change (see figure).

The authors tested their probe on crude-water samples, cellulose paper strips, protein media, and HeLa ("immortal" cancer) cells. The probe molecule exhibits high cell permeability, low toxicity, and good sensitivity in vivo and in protein media.

The probe molecule can be reset to its original state by introducing ethylenediaminetetraacetic acid (EDTA), which binds Hg^{2+} more strongly than does the probe molecule. This allows the probe molecule to be used for as many as 10 cycles. Concentrations can be estimated by comparison with a standard calibration curve.

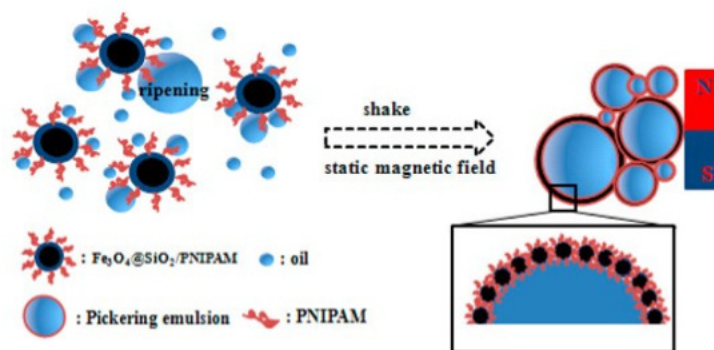
The probe can also serve as a logic gate, which may be useful for making molecular switches and other electronic devices. Adding Hg^{2+} to the probe molecule switches its fluorescence from "OFF" to "ON". Other ions can be added to produce logic circuits with "INHIBIT", "TRANSFER", and "OR" gates. Adding a base such as hydroxide of phosphate resets the circuit so that it can be reused. (*Anal. Chem.* DOI: 10.1021/ac501780z; Nancy McGuire)

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September 8, 2014

Magnetic particles separate oil and water.

Separating oil and water is easy, unless the oil is suspended in wastewater from industrial processes or in contaminated seawater in the aftermath of an oil spill. Membranes and meshes are simple and economical filtering devices, but they have a tendency to foul, and they may cause secondary pollution.



Y. Chen, Y. Bai, and co-workers from the Chinese Academy of Sciences (Lanzhou) and the University of Chinese Academy of Sciences (Beijing) devised stimulus-responsive composite nanoparticles that capture oil droplets suspended in water and facilitate their removal. The particles consist of magnetic iron oxide cores coated with silica ($\text{Fe}_3\text{O}_4@SiO_2$), to which molecular “brushes” made from poly(N-isopropylacrylamide), or PNIPAM, are attached (see figure).

PNIPAM has hydrophilic amide groups and hydrophobic isopropyl groups. The brushlike arrangement of the polymer molecules on the nanoparticle surfaces ensures a large contact area between the polymer molecules and the liquid phase. When the composite particles were added to a toluene–water suspension, shaken for 10 seconds, and then collected using an external magnetic field, a solid-stabilized oil emulsion formed. When the magnetic field was removed, the emulsion rose to the surface.

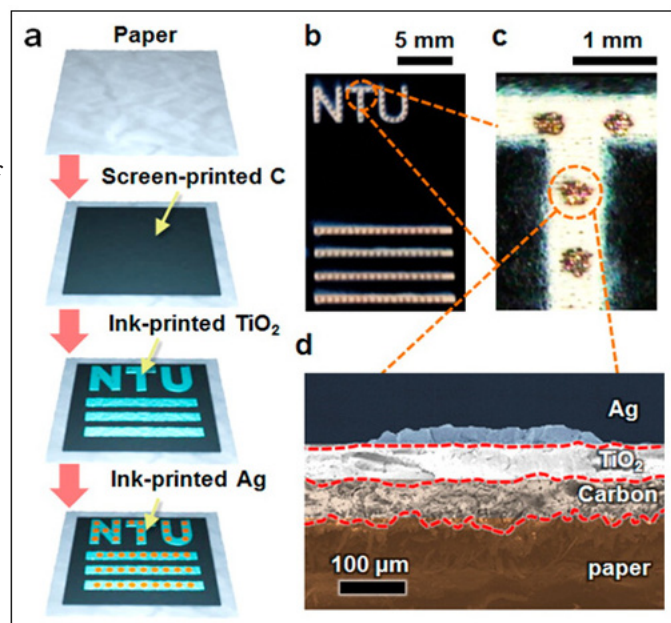
The authors note that the applied magnetic field not only gathers the oil-bearing magnetic particles, but it promotes the formation of larger aggregates. The solid particles prevent the oil droplets from agglomerating to the point where they coalesce, thus stabilizing the oil–particle emulsion for at least three months at room temperature. The composite particles maintained their separation efficiency after five separation–regeneration cycles, which demonstrates their resistance to fouling. (*ACS Appl. Mater. Interfaces* DOI: 10.1021/am504124a; Nancy McGuire)

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August 25, 2014

Smart labels save digital data on paper. Ink on paper is a centuries-old data storage technology, but transferring data from paper to digital storage is often problematic. Y.-C. Liao, S.-C. Lee, J.-H. He, and coauthors at National Taiwan University (Taipei) and King Abdullah University of Science & Technology (Thuwal, Saudi Arabia) went in the other direction: Their printed paper-based memory devices (PPMDs) store digital data on paper. Potential applications include wearable technology, biosensors, and adhesive “smart labels”.

PPMDs are resistive random-access memory (RRAM) devices that consist of metal–insulator–metal layers printed on conventional paper. RRAM is an emerging technology that stores binary data in materials whose resistive states switch from high (off) to low (on), depending on the applied voltage.



The authors claim that an A4 paper-sized PPMD (21 cm x 29.7 cm) provides enough area to store gigabytes of data. The devices operate (with a slight reduction in performance) even when they are wrapped around an AA battery, and they demonstrate reliable data retention and reproducible switching endurance.

Manufacture involves screen-printing a layer of carbon paste onto commercial printing paper, overlaying an inkjet-printed pattern of titania (TiO₂) nanoparticles, and inkjet-printing dots of silver nanoparticle ink on top (see figure). The carbon base layer covers the rough, porous paper surface, ensuring a flat substrate for the overlying patterned layers and bonding them tightly to the paper substrate.

During operation, the silver particles form nanofilaments that extend through the TiO₂ layer to the carbon layer below. By varying the thickness of the TiO₂ layer, the on/off memory window can be tuned over as much as 3 orders of magnitude.

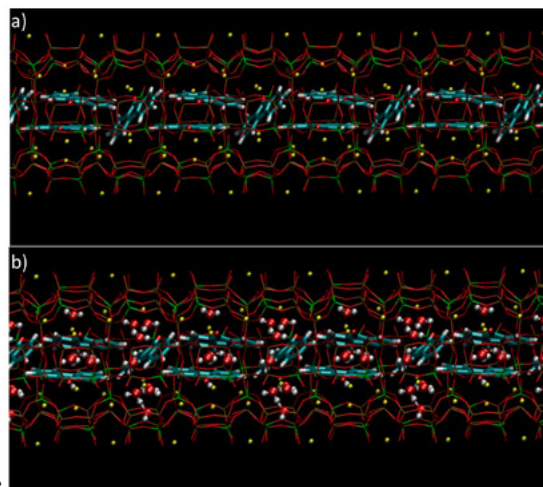
The authors estimate that paper-based RRAM devices could cost less than US\$0.02 each, compared with ≈\$0.05 apiece for conventional components. When the data are no longer needed, the PPMDs can be burned or shredded as a security measure. (*ACS Nano* DOI: 10.1021/nn501231z; Nancy McGuire)

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Dye molecules form nanoladders in zeolite channels. Zeolite frameworks, with their uniform pore systems and molecule-sized openings, make ideal scaffolds for building and supporting assemblies of photoactive molecules. Potential applications of these host-guest systems include microlasers, pigments, optical switches, and antenna systems that mimic those of living plants.

G. Tabacchi and colleagues at the Universities of Modena and Reggio Emilia, Torino, Insubria, and Messina (all in Italy) examined the arrangement of 9-fluorenone dye molecules in the channels of zeolite L. They found that at high loading levels the molecules form quasilinear ladderlike assemblies that run along the zeolite channels. The dye molecules interact strongly with potassium ions in the zeolite host and more weakly with each other.



A hydrogen-bonded network of water molecules surrounds the dye nanoladders and penetrates between their rungs, stabilizing the system without altering the geometry of the dye molecules. The figure shows a model of fluorenone dye molecules enclosed in a zeolite L channel (a) without water and (b) with water.

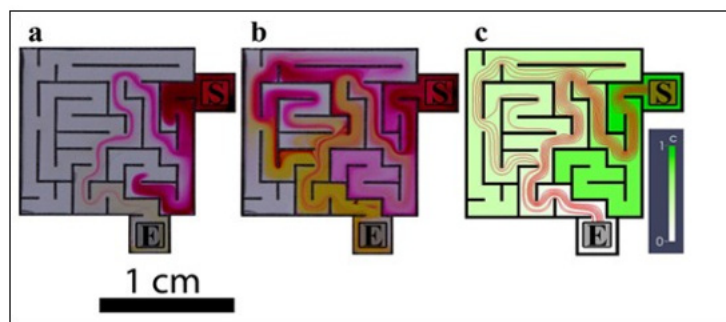
The authors determined that the maximum possible loading is 1.5 dye molecules per zeolite unit cell. They characterized the system by using X-ray diffraction, infrared spectroscopy, thermogravimetry, and theoretical modeling.

At the maximum loading, the most stable arrangement is a ladder with rails made from pairs of parallel 9-fluorenone molecules with their carbonyl oxygen atoms facing the same direction (the syn configuration), aligned along the channel axis, and rungs made from 9-fluorenone molecules tilted $\approx 45^\circ$ with respect to the channel axis. (*J. Phys. Chem. C* DOI: 10.1021/jp505600e; Nancy McGuire)

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August 11, 2014

Dye particles solve maze problems by going with the flow. Maze-solving algorithms are used in navigational problems such as plotting optimal travel routes along city streets. Unfortunately, mathematical methods quickly become difficult and time-consuming as the size and complexity of the maze increases. A faster route to a solution is to use some kind of gradient to drive a fluid stream through a physical maze and use dye tracers to track the flow.



I. Lagzi and coauthors at Meiji University (Tokyo), the University of Edinburgh (UK), the Swiss Federal Laboratories for Materials Science and Technology (Dübendorf), and Budapest University of Technology and Economics used a surface-tension gradient induced by a pH gradient to drive a fluid stream through a complex system of channels toward an exit point. Like previously published methods, this technique can find the shortest path; but it also can find and visualize all possible paths.

The authors caused a water-soluble dye (phenol red) to flow through a maze filled with an alkaline solution of a fatty acid (2-hexyldecanoic acid in aqueous KOH) toward an acid-soaked hydrogel block (HCl in agarose) at the maze exit. The dye method revealed the shortest path through a relatively simple maze after ≈ 10 s (a in the figure); and it showed all possible paths after ≈ 60 s (b). Visualization c illustrates the highest concentration gradients.

The system took ≈ 60 s to find the shortest route between two points in a channel system modeled after a street map of Budapest. The intensity of the dye color was highest for the shortest path, corresponding to the largest surface-tension gradient.

Using a globally imposed field reduced problems with local minima. The dye molecules provided instant visualization of the flow path and eliminated the need for postprocessing. (*Langmuir* DOI: 10.1021/la5018467; Nancy McGuire)

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August 4, 2014

Food and beverage scientists search for the blues. The search for a natural blue food colorant spans all of the biological kingdoms. A. G. Newsome, C. A. Culver, and R. B. van Breemen* at the University of Illinois (Chicago) and Pepsi-Cola (Hawthorne, NY) compiled a review of blue organic compounds derived from plants, animals, fungi, and microbes.

Most natural blue colorants produce less intense coloration than commonly used, synthetic FD&C Blue no. 1. Therefore, higher concentrations of natural blues are required to produce the Blue no. 1 effect, which could produce off-flavors or other undesirable properties. Many natural blues are not stable toward light, heat, or oxidation; and they often change color under acidic conditions.

Some fungi and microbes produce blue alkaloids as a defense mechanism. These compounds could be produced on an industrial scale, but their biological activity makes them unsafe for use in foods and beverages. A few indole alkaloids are blue, but they are often unstable to pH changes and light.

Compounds containing the azulene [5 + 7] ring system have been isolated from fungi and plant essential oils; but they tend to be lipophilic, unstable, and unable to produce a strong blue color. Copper-containing proteins are unstable and change color at low pH.

Many natural blue chromophores have not been identified, often because it is difficult to isolate sufficient quantities for analysis. Other blue colorants are too unstable to be isolated. Many that have been characterized chemically and structurally have not been evaluated for human safety and suitability for food applications.

The authors note that none of the substances they reviewed for this article are likely to meet all the criteria for safety, stability, and suitability for commercial production. The best candidates for new blue color additives, anthocyanin and trichotomine derivatives, will require significant investment for development and regulatory approval. (*J. Agric. Food Chem.* DOI: 10.1021/jf501419q; Nancy McGuire)

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July 28, 2014

Self-folding, nanosized claws grab and hold single cells. A tool for plucking individual cells from solution would facilitate surgery on small blood vessels and analyses of abnormal cell populations. Until now, self-folding “nanogrippers” were too large to select single cells and had limited ability to fold, which prevented them from closing completely around a cell.

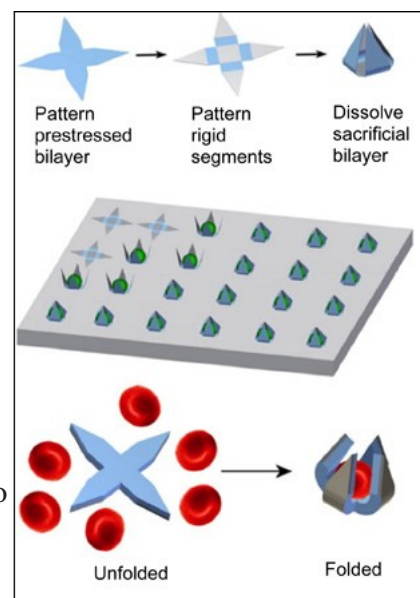
D. H. Gracias and coauthors at Johns Hopkins University (Baltimore) and the US Army Research Laboratory (Adelphi, MD) found a reliable way to produce self-folding anchored or free-floating grippers that can enclose single cells completely. They assembled the grippers from silicon monoxide and silica (SiO and SiO₂)—biocompatible materials that dissolve in biological fluids. The grippers are optically transparent, which helps to view the entrapped cells. The gaps between the gripper arms allow nutrients, waste, and other biochemicals to flow in and out.

Prestressed SiO₂–SiO bilayers are patterned into four-pointed stars, and rigid SiO plates are deposited onto the arms (see figure). When the flat stars are exposed to culture media or biological fluids, the stress in the exposed portions of the bilayer is released, causing the arms to fold upward. Finite element models show that the stress is tunable by using various materials, film thicknesses, and deposition conditions.

The authors used grippers anchored to a substrate to capture single live mouse fibroblasts from a culture media solution. The captured cells remained viable, and the grippers remained anchored to the substrate.

Grippers that were partially released from the substrate entrapped single red blood cells, detached from the substrate, and carried the enclosed cells as free-floating assemblies. This system may be useful for in vivo studies.

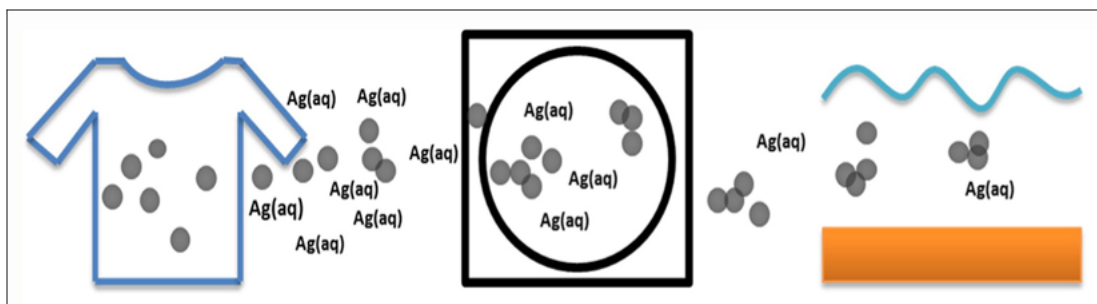
The authors speculate that magnetic elements could guide the grippers through the circulatory system. Patterned biomarkers could allow the grippers to target specific cells in vivo. (*Nano Lett.* DOI: 10.1021/nl500136a; Nancy McGuire)



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July 14, 2014

Not all silver nanoparticles come out in the wash. Soldiers who swelter inside armored vehicles and athletes who work up a sweat in the gym may rely on T-shirts and socks that contain silver nanoparticles (AgNPs) to keep body odor at bay. But the AgNP antibacterial agents that are being used increasingly in consumer products are causing concern about what happens when these particles are released into the environment (see cartoon).



J. Hedberg and co-workers at the KTH Royal Institute of Technology (Stockholm) monitored changes in ionic release and particle properties when samples of uncoated AgNPs were exposed to standard “sweat” solutions (NaCl, urea, and lactic acid), laundry detergent (alcohol ethoxylates, dodecylbenzenesulfonate, and pH buffer), and fresh water (NaHCO₃, KCl, CaCl₂•H₂O, and MgSO₄•7H₂O). They exposed some of their samples to each solution in sequence; others were exposed to only one solution. They also compared laundry detergents with and without zeolites.

The authors found that, in all cases, the amount of silver released was <1% for the single-solution tests and <0.5% of the total amount for the sequential tests. All AgNP samples released comparable amounts of silver into the first solution to which they were exposed, regardless of the solution makeup. The AgNPs exposed to zeolite-containing detergent solutions were an exception: They released far less silver. In particular, samples exposed to artificial sweat, detergent, and fresh water in that order (simulating body contact, washing, and release into the environment) released substantially more silver to the first solution than to the last two.

The authors found evidence that soluble silver on the nanoparticle surfaces was released during exposure to the first solution. The remaining particles were less likely to release silver on the second and third exposures. (*Environ. Sci. Technol.* DOI: 10.1021/es500234y; Nancy McGuire)

June 2, 2014

Laser pulses make quick, economical surface holograms.

Holograms in the visible and near-infrared region offer great promise in security, display, and data-storage applications. The lack of an easy-to-use, inexpensive, and quick method for producing them, however, has limited their practical application. The most commonly used methods for producing holograms often require multiple steps and processing chemicals.

F. da Cruz Vasconcellos, C. R. Lowe, and co-workers at the University of Cambridge (UK) used a single laser pulse to form holographic surface gratings in ink printed onto substrates. The entire hologram production process can be completed within a few minutes, and it can be used to produce two- and three-dimensional holograms on optically transmissive and opaque surfaces. Some examples are shown in the figure. The method requires no photochemical processing.

The researchers printed or spin-coated permanent black ink (with blue, yellow, and red components) onto a flexible plastic substrate. They used a 6-ns pulse from a Nd:YAG laser, with a spot size 1 cm in diameter, to locally heat the coating, which evaporated from the surface in a holographic pattern. They also developed mathematical models to test the effects of various configurations before trying them in the lab.

Reducing thermal diffusion in the light-absorbing material produces greater resolution in the pattern, which can have features comparable in size to the wavelength of the laser light used to produce it. The light-absorbing material can be printed onto the substrate by using inkjet printing, spin coating, stamping, or screen printing. Holograms produced on a transparent substrate are visible from both sides of the substrate.

The authors note that their method can be used with laser light-absorbing inks, dyes, nanoparticles, metals, and biomolecules. They envision that this technology will be integrated into desktop printers or other widely available devices. (ACS *Photonics* DOI: 10.1002/ph400149m; Nancy McGuire)

