this rough, complex landscape. To do that, Wochner *et al.* searched libraries containing a few × 10⁷ sequences. Such populations contain about 10^{-107} of the potentially relevant structures. This is an unimaginably small proportion of all such RNAs, but their search succeeded. How can this be? Even those sequences closely related to R18 RNA are too many to have been thoroughly mapped, despite much prior exploration. As one result, the sequences we know are almost certain to sit far from a major summit of optimality.

Part of the answer lies in the ingenuity and commitment of Wochner *et al.*, who created and wielded new methods. For example, using magnetic microbeads in about 750 μl of oil emulsion (a technique termed "compartmentalized bead-tagging"), they transcribed thousands of clonal copies of a ribozyme, and then selected RNA products made to fluoresce (the resesearchers sorted the beads by the light they emitted). If you love apt and forceful molecular biology, you will love this virtuoso performance, which zeroed in on catalysts with lengthy products. More wizardry followed, including selection of a 5′ core sequence that bound the 5′ end of templates to secure them to the catalytic domain. Screening of experimenter-designed 5′ variants then maximized the ability to use longer primed templates. The result was polymerized products that were ≥ 91 nucleotides long on 0.035% of total primers, annealed to a particularly favorable repetitive template sequence. Finally, the ability to make long products was generalized by recombining certain core mutations and screening for broad performance on several different primer/templates. The final ribozyme produced very accurate templating—just 13 substitutions and deletions in 2200 nucleotides of sequenced RNA products (99.4% correct).

To gather improved accuracy and chain extension into a single experiment, Wochner *et al.* challenged their final ribozyme, tC19Z (see the figure), to make the ribozyme strand of a mini-hammerhead (*5*). It did, lengthening 20% of primer beyond 24 nucleotides, the point at which the mini-hammerhead ribozyme domain is complete. The resulting self-cleaving ribozyme (in combination with a canonical substrate strand) was as effective as the ribozyme synthesized by normal means. For the first time, an RNA-synthesized RNA participated in a second, active, ribozyme.

An RNA polymerase capable of Darwinian evolution is now a large step closer. In the old days (say, 2007), we could template product RNAs that were only 8 to 11% as long as the polymerase. Now we are at 48%. One prediction of the 190-dimensional view is that there is likely to be a route leading up to longer RNA transcripts, if only we can find it. With luck, the very next slopes will take us to Darwinian altitudes, where we have not been before [but see (*6*) for another kind of replication]. However, we also ought to try using the bright tools developed and deployed so effectively by Wochner *et al.* to climb some molehills. We have newly specific access to chain extension. Accordingly, we may be able to reopen the hunt for small RNA polymerases. It was abandoned because irrelevant activities dominated selections (*2*), not because small RNA-RNA polymerases are known, in any sense, to be impossible.

The RNA world likely ended with the invention of translation, allowing peptides to replace active RNAs. In studying this translational finale, it has become evident, in the wake of improved selections, that simple RNAs—as small as five nucleotides—carry out some translational reactions (*7*). Perhaps the time has come to use better-focused, more specific replicase searches on randomized populations of RNA, to look more deeply for a smaller templated phosphodiester transferase, which might have served as the gateway to the RNA world.

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MATERIALS SCIENCE

The Phase Behavior of Interfaces

Martin P. Harmer

Grain boundaries between crystals, which can control materials properties, can interconvert between well-defined equilibrium structures.

Common metal or ceramic objects are made up of many bonded micrometer-scale single crystals, or grains. Their interfaces, called grain boundaries, play a decisive role in determining the properties and processing of almost all engineering materials. Because of their structural and chemical complexities, the description of grain boundaries has lacked a satisfactory conceptual framework, and grain boundaries tend to be viewed as disordered regions with kinetically trapped structures. Recent work has shown that grain boundaries can

Center for Advanced Materials and Nanotechnology and Department of Materials Science and Engineering, 5 East Packer Avenue, Bethlehem, PA 18015, USA. E-mail: mph2@lehigh.edu

be described as interface-stabilized phases (also called interphases or complexions) that are chemically and structurally distinct from any bulk phases (*1–4*). On page 206 of this issue, Baram *et al.* (*5*) extend our understanding of grain boundaries by examining interface structures that form between a gold particle in contact with metal oxide surfaces. They show that these nanoscale interface structures are equilibrium phases that obey thermodynamic rules analogous to those for bulk phases.
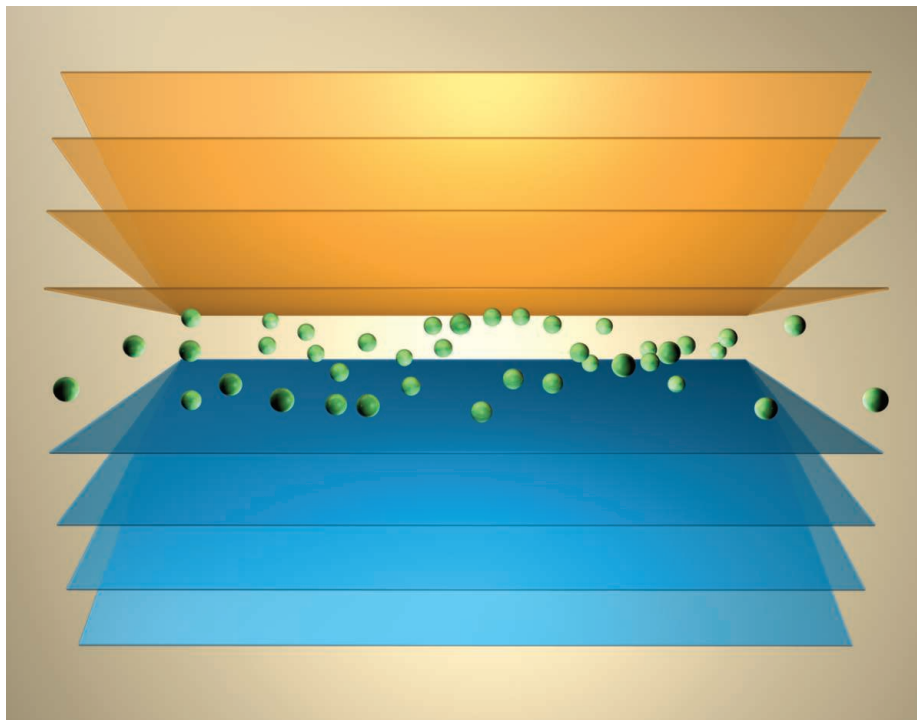
One example of a fundamental problem associated with grain boundaries, and why we need to understand their structure better, is abnormal grain growth. When a material is heated, atoms flow within the grain boundaries, and some grains grow preferentially abnormally large while others disappear. This can create defects and voids inside the material, which can weaken it. Another is embrittlement—impurities can diffuse and segregate into grain boundaries, which impedes the flow of atoms needed to make a material ductile. Conversely, deliberate incorporation of certain atomic elements into grain boundaries can dramatically increase a material's resistance to failure at high temperatures from oxidation or deformation, increasing component lifetime.

The different types of structures that can form at grain boundaries have generally not been described as thermodynamic phases because they are not intrinsically stable as

Defining boundaries. A schematic illustration shows one type of "complexion" phase that can form between different crystals within a material. The crystal planes that make up an interface are shown in blue and orange. The atoms that make up this complexion phase, shown in green, come from impurity, or dopant, elements that were introduced during the processing of the material. The complexion phase does not exist outside the confines of the grain boundary. It can be transformed into one of various other complexion states of matter in order to change the properties of the material. Baram *et al*. report that a nanofilm complexion phase between a gold particle and a metal oxide is a thermodynamically stable phase.

with the availability of the new generation of aberration-corrected scanning transmission electron microscopes of much higher atomic resolution (*8*).

Even if higher atomic resolution can be achieved, the difficulty of accessing internal interfaces makes the characterization of internal grain boundaries more challenging than studies of free-surface interfaces. Free surfaces exhibit layering transitions of adsorbates from monolayers to multilayers that can be formally treated as thermodynamically induced phase changes, which are often represented by surface phase diagrams.

Many exciting opportunities to explore and exploit grain boundary complexions are available given new techniques to observe and characterize them directly, along with the rapidly growing ability to perform realistic quantum-mechanical calculations and simulation methods to predict complexion structures and their transitions (*9*). Verifying the existence and stability range of grain boundary complexions in a wide variety of materials systems, such as metals, ceramics, semiconductors, natural materials, and biomaterials, is an important goal. Measuring and matching the properties with individual complexion types may enable the design of entirely new classes of materials with distinctive combinations of properties, as well as the optimization of the performance of existing materials in applications such as clean energy storage and conversion. The experiments reported by Baram *et al*. set the stage for the development of a rational and robust unifying scientific framework for the understanding of grain boundaries and provides a mechanism-driven approach to design grain boundaries and tailor materials properties (*10*).

stand-alone phases, even though they are thermodynamically stabilized by the internal interfaces between the grains. The term "complexion" clarifies this important distinction in stability behavior between bulk phases, which may coincidentally reside on a grain boundary (see the figure) (*1*–*3*). Each complexion represents an equilibrium state of matter at a crystalline interface, which is neither amorphous nor crystalline. A progressive series of six complexion transitions has been proposed, whereby the discrete number of atomic layers and complexion layer thickness define the number of possible stable complexions. The six different states of complexions that have been distinguished thus far include pure (no layer between the grains), monolayer, bilayer, trilayer, nanofilms (e.g., Baram *et al*.), and wetting films (*1*).

Because complexions are equilibrium features, the way in which conditions and composition determine which complexion forms can be represented on a diagram analogous to bulk phase diagrams (*1*, *2*, *4*). The local boundary energy provides an extra degree of freedom, so boundaries with different complexions can coexist in thermodynamic equilibrium in the same material.

If different complexions have vastly different properties, which is likely to be the case, then the type of complexion that forms should greatly influence materials behavior.

Theoretically, grain boundary complexion phases and their associated transitions were predicted to exist by thermodynamic modeling (*1*–*4*, *6*). The use of conventional high-resolution transmissin electron microscopy (TEM) has directly confirmed the widespread existence of nanofilm complexions in many materials (*7*). Baram *et al*. used such an instrument to study the interfaces between gold droplets and a sapphire (aluminum oxide) surface that was partially coated with calcium-aluminum silicate (anorthite) glass beads. The anorthite formed an intergranular nanofilm that decreased the interfacial energy between the gold particle and the sapphire and that differed from a thicker wetting film.

Despite this demonstration by Baram *et al*. for phase behavior by nanofilm complexions, direct evidence for some of the thinner complexions (especially the bilayers and trilayers) is sparse and controversial. Such studies push the limits of resolution for conventional high-resolution TEM. Fortunately, that is no longer such a limitation

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