Explaining complex metals with polymers

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Analogies and metaphors are widespread in science. We use them to convey difficult concepts to colleagues or when popularizing science to communicate with the general public. Analogies also form an integral part of the scientific process itself (1). Some may even say that science is all about finding analogies between seemingly different phenomena, organizing them using unifying abstract concepts and common models, thereby generalizing these concepts and advancing their understanding. In PNAS, Lee et al. (2) draw a surprising analogy between the principles that govern the formation of ordered phases in soft-matter systems consisting of micelle-forming block copolymers (3), and those underlying the formation of hard solid-state metallic crystals.

Lee et al. (2) study a system of nearly identical diblock copolymers. These are molecules that consist of a pair of different polymer chains of unequal lengths attached at a single point, forming one long double-block chain. Lee et al. (2) observe that under conditions that favor the segregation of the two blocks, groups of about 200 of these copolymer chains self-assemble into spherical micelles. Each micelle resembles a little ball with a core

consisting mostly of one of the blocks, and a corona consisting of the other block. When an initially disordered liquid state, made up of these fuzzy little balls, is cooled down, one observes a phase transition into an ordered state with a simple body-centered cubic (bcc) structure. Upon further cooling, the system undergoes a secondary phase transition into a more complex structure with tetragonal symmetry (that of a square prism), called a Frank–Kasper σ phase (Fig. 1). It is the latter transition from a cubic phase to a lower-symmetry tetragonal phase—which is presumed to be the ground-state configuration that persists down to the lowest temperatures—that is the focus of Lee et al.'s (2) analogy with metals.

The bcc phase consists of cubic cells with one micelle at each corner and an additional micelle at the center of the cube. Because each corner-micelle is shared by eight cubic cells, one has a total of only two micelles per unit cell, with each micelle seeing the same environment. In the σ phase, there are 30 micelles per square-prism cell, with a total of five distinct environments that surround the different micelles. In the bcc phase, Lee et al. (2) find that all of the micelles are

nearly identical, each containing almost exactly 193 diblock copolymer chains. In the σ phase, the five different environments define five volumes with different sizes and shapes, into which the micelles must fit. Because of the energetic cost for having spatial variations in density, the micelles in the low-symmetry phase end up having five distinct sizes, ranging from 176 to 206 chains depending on their volumes. Thus, a redistribution of mass between neighboring micelles must take place at the transition. Indeed, Lee et al. (2) demonstrate that when cooled rapidly, so that the chains do not have sufficient time to diffuse between the micelles, the σ phase does not form. Could there be a process, which would be analogous to the exchange of mass, in similar symmetry-lowering phase transitions in single-component metals, where individual atoms are involved rather than large micelles?

Years ago, Frank and Kasper (4, 5) were attempting to explain the complex structures that appear in metals, using a rather simple geometric requirement for the efficient packing of hard spheres in three dimensions—yet another analogy. Arguing that because the closest arrangement of three hard spheres is a triangle, and that of four spheres is a tetrahedron, Frank and Kasper arrived at four "normal coordination polyhedra" that would typically surround a single sphere. General principles, regarding the different ways one could combine these frequently occurring Frank–Kasper polyhedra into space-filling structures, led Frank and Kasper to discover a number of typical phases, one of which is the σ phase. Frank and Kasper's characterization of metal atoms as hard spheres is extremely successful in explaining many of the structures one commonly observes in metallic alloys. Could there be an equally useful analogy, to soft rather than hard spheres, providing additional insight into the same problem?

Surprisingly, the answers to both of these questions may be positive. Lee et al. (2) contend that the exchange of mass between micelles is analogous to an exchange of charge between atoms in metals. Specifically, the authors argue that different atoms exchange spin-dependent charges as the
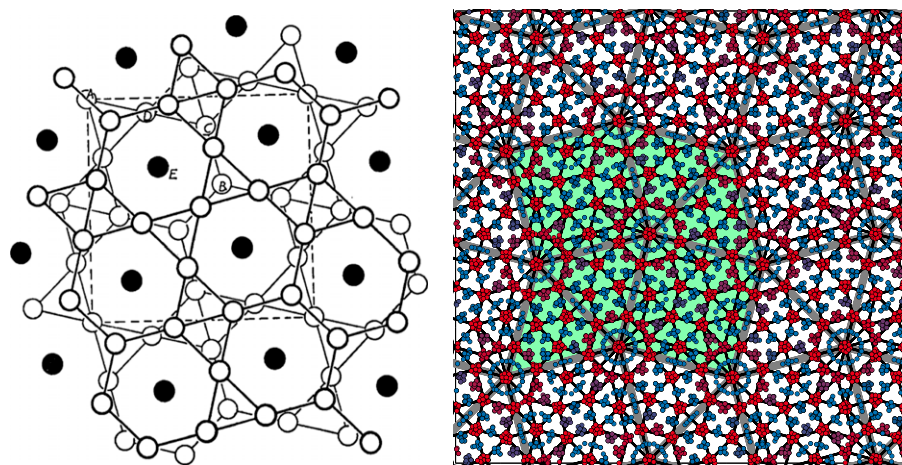

Fig. 1. (*Left*) Sketch of Frank–Kasper σ phase, projected down the axis of fourfold symmetry. The five distinct atomic environments are labeled *A* through *E*. Reprinted with permission from ref. 5. (*Right*) The Frank–Kasper σ phase in the form of a cluster crystal that is obtained in molecular dynamics simulations with ultra-soft isotropic particles. Upon lowering the temperature from the melt, a cluster quasicrystal is formed with 12-fold symmetry. When the temperature is further lowered, one observes a secondary phase transition to this Frank–Kasper σ phase. Thus, the 12-fold quasicrystal takes the role of the periodic bcc phase discussed here. Reprinted with permission from ref. 16.

metal goes through the phase transition. As a result, the low-symmetry phase—even in single-component metals—can effectively be considered as an intermetallic alloy, consisting of inequivalent atomic sites, with varying coordination, different magnetic moments, and most importantly different effective atomic radii. Like micelles, the individual atoms have at their disposal a mechanism by which they can adjust their effective size as they reposition themselves in the low-symmetry crystalline arrangement.

Lee et al. (2) make an even more intriguing analogy between the mechanisms that drive the symmetry-lowering phase transitions in the two systems. They speculate that what drives the phase transition in the polymer system is the strong preference of the micelles to be perfectly spherical. As the temperature is lowered the shape of the micelle becomes more sharply defined. As thermal fluctuations decay, both the interface between the core and the corona and the outer surface of the corona sharpen, making the micelles more rigid and deviations from sphericity more costly in energy. Indeed, Lee et al. (2) demonstrate that the five different polyhedral cells that individual micelles occupy in the low-temperature σ phase are more spherical, on average, than the single truncated octahedral cell occupied by all of the micelles in the high-temperature bcc phase. This is a plausible and interesting suggestion that should be tested quantitatively, especially in light of seemingly contradicting arguments, such as that of Ziherl and Kamien (6), who suggest that increased sphericity, which reduces the contact area between soft particles, would increase the entropy and therefore be favored at the high temperature side of the phase transition. Nevertheless, assuming that this is indeed the mechanism that drives the phase transition here, what would be the analogy with atoms in a metal?

The analogy that Lee et al. (2) propose is not to spheres formed by the atoms themselves in position space, but rather to the so-called Fermi surface, formed by the highest-energy electrons in momentum space. In the disordered liquid phase, which is isotropic, the momenta of the fastest electrons all have the same magnitudes regardless of their direction. Thus, when plotted in momentum space, they define a surface of constant radius: a sphere. In the ordered crystalline phase the isotropic symmetry is broken and the Fermi sphere turns into a more general surface. The effect of the anisotropic ionic potential is most conveniently represented by a polyhedron in momentum space, indicating positions where the potential induces gaps in the electronic spectrum as a function of momentum. This polyhedron is called a Brillouin zone when

the ionic potential is periodic, and a Jones zone, when it is not. In the latter case, the number of electronic states at the zone boundary is suppressed but not necessarily down to zero, forming a pseudogap.

A well-known mechanism for the stabilization of metals, which depending on the context is named either after William Hume-Rothery or after Rudolf Peierls, relies on the delicate interplay between the electronic configuration and the geometry of the crystal. It may be beneficial for atoms to shift their positions, even at the cost of straining the crystal, as long as the correspondingly shifted (pseudo)-gap, positioned according to the new shape of the Jones zone, is better aligned with the Fermi surface, which is more effective when the Jones zone is more spherical. This allows the most-energetic electrons to substantially lower their energy, as the system avoids the energetic penalty of placing these electrons above the (pseudo)-gap at the Jones zone boundary.

Lee et al. (2) draw an analogy between the sharpening of the micelle surface and its core-corona interface and the sharpening of the Fermi surface at low temperature, saying that the preference for sphericity of these two surfaces is what drives the phase transition in both cases. It is hard to stress enough how different these two surfaces are—one defined in position space and the other in momentum space—and consequently how intriguing and surprising is the analogy between them. Whereas the surface of a micelle is a local property of just a single micelle, the Fermi surface is a global property, which in principle takes into account all of the electrons in the metal.

Analogies are often made between soft-matter systems and hard-matter solids, yet most are not as specific as this. The analogy here is between the symmetry breaking at the bcc to σ phase-transition in diblock copolymers, mediated by the exchange of mass, and the symmetry breaking in certain metals and alloys, mediated by the exchange

of charge. The tendency of block-copolymer micelles to form spheres in position space is compared with the tendency of metals to form spherically symmetric Jones zones in momentum space. The competition between these tendencies and the need to fill space uniformly is then said to be responsible for the observed phase transitions in both cases. Further quantitative work is still required to establish the merit of this analogy, and to strengthen the points of connection between the two systems. It may prove beneficial to expand the analogy and add considerations of entropy, thereby enabling a comparison between the higher-temperature ordered phases that form directly upon cooling from the melt as well. In any case, if valid, the analogy could be very helpful, as it would allow one to use block polymers to elucidate and explain the formation of complex metallic phases, which continue to pose challenging scientific questions to this day (7).

Particularly interesting and challenging are quasicrystals, a special class of crystals that are not periodic (8, 9), and therefore quite difficult to study. Quasicrystals have been observed in metallic alloys since their discovery more than three decades ago (10), and in the last decade also in a variety of soft-matter systems ranging from dendrimeric micelles and star polymers to nanoparticles in solution (11–13, and references therein). The proposed analogy—valid at the moment only for low-temperature phases where entropy is unimportant—may be irrelevant for most metal-alloy quasicrystals, as they possess mostly 5-fold and 10-fold rotational symmetry, whereas soft-matter quasicrystals are predominantly 12-fold symmetric. Nevertheless, it may help elucidating the physics of those few metallic alloys that do form 12-fold quasicrystals, like NiCr (14) and VNi/VNiSi (15), and perhaps explain why they are so different from the others.

1 Crease RP (2000) Physics, metaphorically speaking. *Physics World* 13(11):17.
2 Lee S, Leighton C, Bates FS (2014) Sphericity and symmetry breaking in the formation of Frank–Kasper phases from one component materials. *Proc Natl Acad Sci USA* 111:17723–17731.
3 Bates FS, Fredrickson GH (1999) Block copolymers—Designer soft materials. *Physics Today* 52(2):32–38.
4 Frank FC, Kasper JS (1958) Complex alloy structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallogr* 11:184–190.
5 Frank FC, Kasper JS (1959) Complex alloy structures regarded as sphere packings. II. Analysis and classification of representative structures. *Acta Crystallogr* 12:483–499.
6 Ziherl P, Kamien RD (2001) Maximizing entropy by minimizing area: Towards a new principle of self-organization. *J Phys Chem B* 105(42):10147–10158.
7 Dubois J-M, Belin-Ferre E (2010) *Complex Metallic Alloys: Fundamentals and Applications* (Wiley-VCH, Weinheim).
8 Lifshitz R (2007) What is a crystal? *Z Kristallogr* 222(6):313–317.

9 Lifshitz R (2011) Symmetry breaking and order in the age of quasicrystals. *Isr J Chem* 51:1156–1167.
10 Shechtman D, Blech I, Gratias D, Cahn JW (1984) Metallic phase with long-range orientational order and no translational symmetry. *Phys Rev Lett* 53(20):1951–1953.
11 Lifshitz R, Diamant H (2007) Soft quasicrystals—Why are they stable? *Philos Mag* 87(18-21):3021–3030.
12 Ungar G, Percec V, Zeng X, Leowanawat P (2011) Liquid quasicrystals. *Isr J Chem* 51:1206–1215.
13 Dotera T (2011) Quasicrystals in soft matter. *Isr J Chem* 51:1197–1205.
14 Ishimasa T, Nissen H, Fukano Y (1985) New ordered state between crystalline and amorphous in Ni-Cr particles. *Phys Rev Lett* 55(5):511–513.
15 Chen H, Li DX, Kuo KH (1988) New type of two-dimensional quasicrystal with twelvefold rotational symmetry. *Phys Rev Lett* 60(16):1645–1648.
16 Barkan K, Engel M, Lifshitz R (2014) Controlled self-assembly of periodic and aperiodic cluster crystals. *Phys Rev Lett* 113(9):098304.