Frank Kasper Phases of Squishable Spheres and Optimal Cell Models

1) **Selective assemblies of giant tetrahedra via precisely controlled interactions**, M. Huang, C.-H. Hsu, J. Wang, S. Mei, X. Dong, Y. Li, M. Li, H. Liu, W. Zhang, T. Aida, W.B. Zhang, K. Yue and S. Z. D. Cheng, *Science* **348**, 424-8 (2015).

2) **Sphericity and symmetry breaking in the formation of Frank-Kasper phases from one component materials**, S. Lee, C. Lieghton and F. S. Bates, *Proc. Nat. Acad. Sci. USA* **111**, 17723-31 (2014).

3) σ **phase formed in conformationally asymmetric AB-type block copolymers**, N. Xie, W. Li, F. Qui, A.-C. Shi, *ACS MacroLetters* **3**, 906-10 (2014).

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Optimal sphere packings as models of matter date back to Kepler [1], who conjectured that hexagonally-close packed structures (e.g. FCC, HCP lattices) are maximal-density arrangements of rigid spheres. That conjecture is now proven to be correct [2] and generally accepted to explain the stability of hexagonally-close packed order in many materials, from colloids to metals. By comparison, understanding the optimal packing of highly-deformable, *squishable* spheres, and its implications for self-organized soft matter, remains an active area of inquiry.

Consider a schematic of squishable spherical domains, self-assembled from many amphiphillic block copolymer molecules, shown in Fig. 1A. In neat systems, where solvent is unavailable to fill gaps, idealized spheres must be deformed, squished, to fill the interstitial voids and distribute mass roughly evenly throughout the volume, as is generically favored by van der Waals forces. The resulting structure is composed of self-assembled domains occupying lower symmetry cells, related to the Voronoi cells of the lattice. Finding the optimal lattice therefore reduces to problem of determining the space-filing polyhedra that minimize the free energy cost to squish the ideally-spherical assembly into the appropriate set of lower symmetry, polyhedral cells. What is that cost? In 2000, Ziherl and Kamien proposed that a natural term in that cost is proportional to the area of those cells [3], and hence, with the additional assumption of constant cell volume, that optimal soft sphere lattices can related to optimal dry foams. As a standard measure, consider the *reduced area* $\mathcal{A}(X) = A(X)/A_{\rm Sph}$, where $A(X)$ is the area of the polyhedral cells of partition X and $A_{\rm Sph}$ is the area of an equal-volume sphere (such that $\mathcal{A}(X) > 1$). In 1994, Weaire and Phelan showed that the equal-volume partition provided by the A15 lattice has the lowest known area with $\mathcal{A}(\text{A15}) = 1.0935$ [4]. Based on Weaire and Phelan's result–which disproved Kelvin's conjecture that BCC optimizes cell area ($\mathcal{A}(\text{BCC}) = 1.0973$) and stands to this day–Ziherl and Kamien developed a heuristic model to rationalize the appearance of A15 lattice in amphiphilic dendron assemblies [5].

Recent studies of a broader class of assemblies shed new light on this optimal cell shape argument and the ability of soft systems, more generally, to form lattice symmetries beyond those typically encountered in single component systems, such as FCC or BCC. A15 belongs to a class of lattices known as Frank Kasper (FK) phases, also known as tetrahedrally-closed packed (TCP) lattices because four adjoining Voronoi cells meet at a common vertex (hence, compatible with Plateau's rules). FK lattices were originally proposed as models of metal alloys [6] as they possess multiple cells, built from different combinations of pentagonal and hexagonal faces, at varying stoichiometry. For example, A15 possess two cell types: 12-hedra for lattice positions at the centers and corners of the cubic unit cell; 14-hedra for each of two lattice positions on the faces of the cubic unit cell (see Fig. 1B). Given that A15 and other Frank Kasper phases are composed of two or more fundamentally distinct sphere-like domains, it is counterintuitive that these phases form at all in single-component systems, such as dendrimers, or branched diblock copolymers [7].

New results on the assembly of a wholly new class of molecular amphiphiles, by Huang *et al* (paper 1), provides a more direct assessment of the asymmetry possible in Frank Kasper assemblies of squishy spheres. The authors have synthesized what they call "giant tetrahedra" (which are, in fact, a few nm in size), by chemical attachment nanoscale cubes on tips of a tetrahedral, rigid molecular frame. These nanocubes can be selectively functionalized by hydrophobic or hydrophilic groups. By altering the hydophobic/hydrophillic ratio and the strength of hydrophobic interactions, the authors effectively alter the local geometry of building block packing that minimizes contact between hydrophobic/hydrophillic domains, as in classical amphiphiles. Over the range of hydrophobic/hydrophilic nanocube ratios, these apparently "rigid" building blocks form a remarkably spectrum of mesodomain phases (periodic spheres, cylinders, double gyroids) typically formed only by flexible systems like diblocks, clearly requiring a significant deformability of their local arrangements. For a ratio of 1:3 hydrophobic:hydrophilic nanocubes, the nanotetrahedra form spherical domains, and these domains form cubic superlattices which are either A15 or BCC for, respectively, stronger or weaker hydrophobic interactions. By high-resolution electron microscopy, the authors directly measure the asymmetry in size and shape of distinct spheres in these phases. In the A15 phase, spheres in the 14-hedral cells are measured to mean diameters that are 10% larger than those in the 12-hedral cells. They estimate that 14-hedral spheres contain 50-65 amphiphiles while smaller 12-hedral spheres contain 40-50. Along with the optimal area principle of the Weaire-Phelan foam, Huang *et al* argue that the ability of the somewhat "flattened" 14-hedral spherical

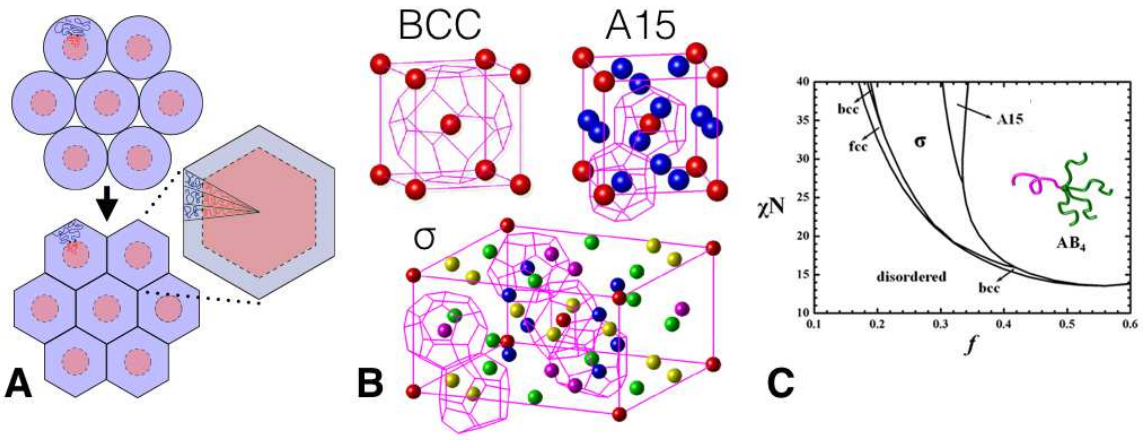

FIG. 1: In (A) and schematic of "squishing" ideally spherical, self-assembled domains of diblock copolymers into spacing filling cells. In (B), competing arrangements of squishy spheres with distinct color making distinct lattice positions with polyhedral Wigner Seitz cells shown pink. In (C) the phase diagram of asymmetry "miktoarm" star diblocks showing stable ranges of all three lattices shown in (B). (B) and (C) are adapted from Xie *et al*, *ACS MacroLetters* **3**, 906 (2014).

domains to accommodate more volume (as hydrophobic/hydrophillic segregation increases) without exceeding a maximal caliper allowed by the rigid building blocks is crucial to the A15 in this system, in line with previous arguments about the stability of Frank Kasper structures in models of mixtures of symmetric/asymmetric soft spheres [8].

Paper 2, by Lee, Creighton and Bates, takes a similar point of view about the stabilizing effect of volume asymmetry of self-assembled spherical domains, but comes to a different conclusion. This study is focused on experimental results of linear diblock copolymers, polyisoprene-*b*-polylactic acid (or PS-PLA), forming a cubic sphere phase, as in the schematic of Fig. 1A. According to the authors, what distinguishes this system from the many other sphere-forming diblock systems to date is a combination of low-molecular weight while, at the same time, achieving a relatively strong degree of inter-block repulsion in the molten state. With decreasing temperature this sample (which is 22% PLA) ordered into BCC then a σ-lattice of spherical domains (Fig. 1B). The σ-phase is another FK lattice with an even more complex structure than BCC: 24 sphere positions in a cubic repeat, corresponding to 8 fundamentally distinct Voronoi cells (e.g. inequivalent domain symmetries).

Lee *et al* argue that the at lower temperature, strong-stretching of short blocks imparts an especially high free-energy penalty for forming non-spherical domains, which in turn accounts for the stability of σ. In their argument, they describe "sphericity" in terms of the *isoperimetric quotient* of the Voronoi cells, $f(X) \equiv 36\pi V(X)^2/A(X)^3$. Since, $f(X)^{-1/3} = \mathcal{A}(X)$ it would seem that this is back to the Ziherl and Kamien argument again and the A15 lattice should have the smallest "sphericity" according the Weaire-Phelan optimal foam. Not quite. Lee *et al* construct the Voronoi cells according to the sphere centers, more specifically, they find the standard Wigner Seitz polyhedra bounded by the planes bisecting the neighbors surrounded a lattice position. By taking the appropriate volume-weighted average of $f(X)$ they show that not only does σ beat BCC, but it also beats A15 (according to this calculation, $\mathcal{A}(\sigma) = 1.0946 < \mathcal{A}(A15) = 1.0949$). At first glance this appears to contradict to optimality of the Weaire-Phelan structure, which has yeas ago been tested against σ as well as a broader family of TCP lattices (for equal volume cells, $\mathcal{A}(\sigma) = 1.0945 > \mathcal{A}(A15) = 1.0935$) [9]. In fact, these two calculations are comparing subtly different cell geometries. In the foam problem where A15 is the undisputed king, the volume of each cell is held constant, while the shape of each face relaxes (e.g. curves) to lower area, while the Wigner-Seitz cells 1) have planar (unrelaxed) faces and 2) do not enclose the same volume. Indeed, Lee *et al* cite the roughly 10% range of volume variation of the σ cells, and the implicit mass exchange of chains between spherical domains along the lines of measured explicitly by Huang *et al*, as an stabilizing effect, as it leads to "more spherical" cells than competitor structures.

But if both the equal-volume (foam) and Wigner-Seitz (planar face) cells are only partially relaxed, where does this leave us as far the optimal lattice of "squishable" spheres? A new theoretical study (paper 3), by Xie *et al*, provides some important and needed insight into the "tug of war" between A15 and σ, by showing that both phases (along with BCC) appear in the same phase diagram of a "elasticity-asymmetric" AB_n (miktoarm star) diblocks (AB_4 shown in Fig. 1C). This study uses self-consistent field (SCF) theory to directly compute the free energies of competing lattice arrangements of spheres (and other diblock morphologies) without imposting any assumptions about the detailed shapes and volumes of spherical domains. Increasing entropic stiffness of the coronal domain (by increasing number of B arms, n), opens up a large composition window of stable sphere morphologies [12]. Previous SCF results showed that that A15 becomes stable over the more typical BCC packing in this asymmetric regime [10, 11]. In their paper,

Xie *et al*, checked a much broader set of Frank Kasper structures by SCF and showed that σ phase *also* becomes lower free energy than BCC. In fact, in weakly asymmetric cases (say $n = 2$) the σ phase more or less usurps the erstwhile predicted region of A15 stability. Only at large molecular asymmetries ($n \gtrsim 3$) do they find a window of stable A15 before spheres are overtaken by cylinders at larger A block fraction, f. Their results show that σ appears at *intermediate* conditions to the previously identified stable lattices: with increasing f they find the generic sequence BCC $\rightarrow \sigma \rightarrow$ A15 ($\rightarrow$ cylinders).

This sequence of lattice stability identified by Xie *et al* seems to me a particular important result, though how the stability of these phases relates to optimal geometric principles of the lattice partitions remains an open question. Taken together, papers 1 and 2 show the importance of relaxing the cell relative volumes of distinct sphere positions in the lattice to account for the the very likely possibility of mass exchange between the domains. However, *without constraints on the relative changes of cell volumes*, optimizing the cell areas alone – as in the Kelvin problem – becomes an ill-posed problem. A properly defined geometric model of squishy sphere packing must, therefore, include a natural penalty for volume deviations, as well as area deviations, from the spherical ideal.

To date, no study has compared the cell areas (as proxies of free energies) of BCC, A15 to σ and other FK structures, subject to an additional cost for volume exchange between cells. Moreover, the relative importance of volume relaxation and cell-wall shape relaxation in this competition is unresolved. One possible model that naturally incorporates a penalty for cell volume variation, mentioned by Xie *et al*, applies to the "polyhedral interface limit" of diblock domains when the AB interface perfectly copies the shape of the surrounding Voronoi cell [12], which requires optimization of area and and a geometric measure of chain stretching in the cells. Of course, this measure, the second-moment of cell volume, only holds as a model of Gaussian chain stretching, and will not apply to molecular geometries beyond flexible chain polymers. Nevertheless, revisiting this, or other generalizations of the minimal area model of squishable spheres, via the same optimization methods originally applied to disprove Kelvin's conjecture could provide a well-defined path forward for understanding geometric selection mechanism between nearly degenerate, competing FK structures, or maybe even, quasicrystalline assemblies [13].

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[1] T. Aste and D. Weaire, *The Pursuit of Perfect Packing* (Taylor and Francis, New York, 2008), 2nd Ed.

[2] T. C. Hales, "Cannonballs and honeycombs", *Not. Am. Math. Soc.* **47** 440 (2000) .

[3] P. Ziherl and R. D. Kamien, "Soap Froths and Crystal Structures", *Phys. Rev. Lett.* **85**, 3528 (2000); P. Ziherl and R. D. Kamien, "Maximizing Entropy by Minimizing Area: Towards a New Principle of Self-Organization", *J. Phys. Chem. B* **105**, 10147 (2001).

[4] D. Weaire and R. Phelan, "A counter-example to Kelvin's conjecture on minimal surfaces", *Philos. Mag. Lett.* **69**, 107 (1994).

[5] V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, "Rational Design of the First Spherical Supramolecular Dendrimers Self-Organized in a Novel Thermotropic Cubic Liquid-Crystalline Phase and the Determination of Their Shape by X-ray Analysis", *J. Am. Chem. Soc.* **119**, 1539 (1997).

[6] F. C. Frank and J. S. Kasper, "Complex Alloy Structures Regarded as Sphere Packings. II. Analysis and Classification of Representative Structures", *Acta Cryst.* **12**, 483 (1959).

[7] B.-K. Cho, A. Jain, S. M. Gruner and U. Weisner, "Mesophase Structure-Mechanical and Ionic Transport Correlations in Extended Amphiphilic Dendrons", *Science* **306**, 1598 (2004).

[8] C. R. Iacovella, A. S. Keys and S. C. Glotzer, "Self-assembly of soft matter quasicrystals and their approximants", *Proc. Nat. Acad. Sci. USA* **108**, 20935 (2011).

[9] R. Phelan, "Generalizations of the Kelvin problem and other minimal problems", in *The Kelvin Problem*, ed. D. Weaire (Taylor & Francis, London, 1996).

[10] G. M. Grason, B. A. DiDonna and R. D. Kamien, "Geometric Theory of Diblock Copolymer Phases," *Phys. Rev. Lett.* **91**, 058304 (2003); G. M. Grason and R. D. Kamien, "Interfaces in Diblocks: A Study of Miktoarm Star Copolymers", *Macromolecules* **37**, 7371.

[11] G. M. Grason, "The packing of soft materials: Molecular asymmetry, geometric frustration and optimal lattices in block copolymer melts" **433**, 1 (2006).

[12] P. D. Olmsted and S. T. Milner, "Strong-Segregation Theory of Bicontinuous Phases is Block Copolymers," *Phys. Rev. Lett.* **72**, 936 (1994).

[13] X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey and J. K. Hobbs, "Supramolecular dendritic liquid quasicrystals", *Nature* **428**, 157 (2004).