

## Soap Froths and Crystal Structures

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**Abstract.** We discuss the physics and mathematics of sphere packing and minimal surfaces and use these to explain the crystal symmetries found in macromolecular and supramolecular micellar materials and charged colloids. In the case of molecular assemblies, we argue that the packing entropy of the hard micellar cores is frustrated by the entropic interaction of their brush-like coronas. The observed crystal structures correspond to the Kelvin and Weaire-Phelan minimal foams. We show that these structures are stable for reasonable areal entropy densities.

Over 400 years ago, Kepler conjectured that the densest way to pack equal-sized hard spheres was in a face-centered-cubic (FCC) or equivalent hexagonal-close-packed (HCP) lattice. Though this conjecture was thought to be correct, it was not until recently that a rigorous proof was presented [1]. Because a denser packing implies a greater free volume for hard spheres, they will pack in one of these dense lattices to maximize entropy or minimize free energy. However, a new class of highly monodisperse dendritic polymers [2] have been characterized. Though the monodendrons form spherical micelles, these spheres assemble into an A15 lattice with  $Pm\bar{3}n$  symmetry. This lattice has the same density as the simple cubic lattice and is very far from dense packing.

We have proposed an explanation of the equilibrium structure by appealing to the mathematics of minimal surfaces [3, 4]. We view the dendritic micelle as a hard sphere of diameter  $\sigma$  with a soft, repulsive corona. We would then expect our conclusions to hold for a large class of materials with similar morphology, e.g. diblock copolymer micelles [5], nanoparticles decorated with hydrocarbon chains [6], and charged colloids [7, 8]. If we consider a sample of dendritic micelles at a fixed number density  $\rho$  then in a fixed volume  $V$ , there are  $N = \rho V$  spheres and so

$$V_{\text{corona}} = V - \frac{\pi}{6}\sigma^3\rho V = V \left[ 1 - \frac{\pi\sigma^3}{6}\rho \right] \quad (1)$$

is the volume left over the soft coronas. This coronal volume shrouds the hard spheres forming a thick surface of area  $A$  and thickness  $\tau$ . Since

$$A\tau = V_{\text{corona}} \quad (2)$$

is fixed, it follows that to minimize the repulsive potential or maximize  $\tau$ ,  $A$  should be minimized. The area per micelle depends on the shape of the Voronoi cell and

scales as the volume  $V_M^{2/3} = \rho^{-2/3}$ :

$$A_M \equiv \frac{A}{N} = \frac{1}{\tau} \left[ \rho^{-1} - \frac{\pi\sigma^3}{6} \right] \quad (3)$$

$$= \gamma V_M^{2/3} = \gamma \rho^{-2/3} \quad (4)$$

This last equality allows us to write the separation  $\tau$  in terms of the density and the geometric quantity  $\gamma$ . We see that to maximize  $\tau$  at fixed density we should minimize  $\gamma$ .

The problem of minimizing the total area of equal volume cells that fill space was first proposed by Kelvin [9]. He conjectured that the body-centered-cubic (BCC) lattice of *orthic tetrakaidecahedra* (or the more modern *orthic decatetrahedra* [10]) minimized the area of the cells. However, in 1994, Weaire and Phelan [11] discovered that the A15 lattice, composed of equal volume Goldberg dodecahedra and dodecahedra, had a still smaller surface area. As of this writing, it is not known whether there is a structure with a yet smaller area. However, based on this discovery, we see that the repulsive energy of the coronas is smaller for the A15 lattice than the FCC or BCC lattice. Quantitatively we have  $\gamma^{\text{FCC}} = 5.345$ ,  $\gamma^{\text{BCC}} = 5.306$ , and  $\gamma^{\text{A15}} = 5.288$ , while the volume fractions of close-packed FCC, BCC and A15 lattices are  $\rho_{\text{FCC}} = 0.74$ ,  $\rho_{\text{BCC}} = 0.68$  and  $\rho_{\text{A15}} = 0.52$ . Therefore there is an intrinsic frustration between maximizing the free volume and minimizing the surface area or, in other words, between the entropy of the hard cores and the interactions of the coronas.

We have found that for physical values of the interaction parameters, the A15 lattice can be more stable than either the BCC or FCC lattice [3, 4] and that the BCC lattice is more stable than FCC for charged colloids at low salt concentrations [8]. This trend has been born out by experiment [5, 6, 7] and by simulation [4, 10].

Future work will focus on the relative stability of non-cubic lattices [12].

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## References

- [1] T.C Hales, *Discrete Comput. Geom.* **25** (2001) 1.
- [2] V.S.K. Balagurusamy, G. Ungar, V. Percec, and G. Johansson, *J. Am. Chem. Soc.* **119**, 1539 (1997).
- [3] P. Ziherl and R.D. Kamien, *Phys. Rev. Lett.* **85**, 3528 (2000) [cond-mat/0007256].
- [4] P. Ziherl and R.D. Kamien, *J. Phys. Chem. B* **105**, 10147 (2001) [cond-mat/0103171].
- [5] G.A. McConnell, A.P. Gast, J.S. Huang, and S.D. Smith, *Phys. Rev. Lett.* **71**, 2102 (1993); G.A. McConnell and A.P. Gast, *Phys. Rev. E* **54**, 5447 (1996).
- [6] R.L. Whetten, M.N. Shafigullin, J.T. Khoury, T.G. Schaaff, I. Vesmar, M.M. Alvarez and A. Wilkinson, *Acc. Chem. Res.* **32**, 397 (1999).
- [7] E. B. Sirota, H.D. Ou-Yang, S.K. Sinha, P.M. Chaikin, J.D. Axe, and Y. Fujii, *Phys. Rev. Lett.* **62**, 1524 (1989).
- [8] W. Kung, P. Ziherl and R.D. Kamien, *Phys. Rev. E* **65**, 050401(R) (2002) [cond-mat/0111313].
- [9] W. Thomson, *Phil. Mag.* **24**, 503 (1887).
- [10] C.N. Likos, N. Hoffman, H. Löwen and A.A. Louis, *J. Phys. Cond. Mat.* **14**, 7681 (2002) [cond-mat/0205109].
- [11] D. Weaire and R. Phelan, *Phil. Mag. Lett.* **69**, 107 (2004).
- [12] W. Kung, P. Ziherl and R.D. Kamien, *unpublished* (2002).

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