Soap Froths and Crystal Structures

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We propose a physical mechanism to explain the crystal symmetries found in macromolecular and supramolecular micellar materials. We argue that the packing entropy of the hard micellar cores is frustrated by the entropic interaction of their brushlike coronas. The latter interaction is treated as a surface effect between neighboring Voronoi cells. 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.

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Dendritic polymers [1–3], hyperbranched star polymers [4,5], and diblock copolymers [6,7] represent a new class of molecular assemblies all of which form a variety of crystalline lattices, many of which are not close packed. These assemblies are all characterized by compact cores and brushlike, soft coronas. These systems might be modeled by treating the micelles as sterically interacting hard spheres and it would follow that their crystalline phases should be stackings of hexagonal-close-packed (hcp) layers. Recently [8] it has been shown that the face-centered-cubic (fcc) lattice maximizes the total entropy and so hard-sphere crystals should form fcc structures. Note that the entropic difference between the various hcp lattices is a *global* issue: the local arrangement of spheres is the same for all close-packed variants and thus the lattice cannot be predicted from nearest-neighbor interactions. In order to understand the richness of crystal symmetries in the micellar systems, we propose an additional global consideration: we add an interaction proportional to the interfacial surface area between the cages which contain each micelle (Voronoi cells). Though approaches based on self-consistent field theory and two-body interactions can yield non-close-packed lattices [9,10], we propose a universal explanation for a host of new structures and present a new paradigm for the rational design and control of macromolecular assemblies [11].

The interfacial interaction arises through the entropy of the brushlike coronas of the micelles. Because of constraints on their conformations, the brushes suffer an entropic penalty proportional to the interfacial area between the Voronoi cells surrounding each sphere. Thus they favor area-minimizing structures, precisely the type of structures that dry foams might make. Over a century ago, Lord Kelvin proposed that a body-centered-cubic (bcc) foam structure had the smallest surface-to-volume ratio [12], but in 1994 Weaire and Phelan found that a structure based on the A15 lattice [13] was more efficient. We note that neither the bcc nor A15 structures are close packed and thus there is a fundamental frustration between the hard-core volume interaction and the surface interaction due to overlapping soft coronas.

For concreteness, in this paper we focus on structures observed in a family of dendrimer compounds consisting of a compact poly(benzyl ether) core segment and a diffuse dodecyl corona [1,2]. These conical dendrimers self-assemble in spherical micelles which subsequently arrange into the A15 lattice (Fig. 1). The interaction between the micelles is primarily steric, i.e., repulsive and short range. The micellar architecture suggests that the potential is characterized by three regimes. At large distances, the micelles do not overlap and the interaction vanishes. As the coronas begin to overlap, the entropy of the brushlike coronas decreases, which gives rise to a soft repulsion between the micelles. Finally, at small separations the coronas begin to penetrate the compact cores: this is very unfavorable and gives rise to hard-core repulsion. This energy landscape is in qualitative agreement with recent, detailed molecular dynamics simulations [14].

Although both originate in steric interaction, the two repulsive regimes are characterized by very different functional behaviors. The hard part of the potential results in a

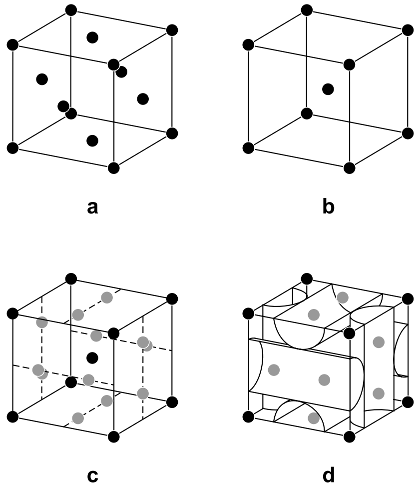

FIG. 1. Various lattices: (a) Face-centered cubic, (b) body-centered cubic, (c) A15 lattice, and (d) columnar representation of A15 lattice. In the A15 lattice, columnar and interstitial sites are drawn in grey and black, respectively.

restricted positional entropy of the micelles which depends on the free volume, the difference between the actual and the hard-core volumes. The soft part comes from the decreased orientational entropy of the chains within the overlapping coronas. The matrix of overlapping coronas can be thought of as a compressed bilayer and thus the free volume may be written as a product of the interfacial area A and the average spacing between the hard cores d so that at any given density

$$Ad = \text{const}. \tag{1}$$

Though this approximation ignores the curvature of brushlike coronas, the dendrimers are relatively close and we expect this constraint to hold in this system. Since the repulsion decreases monotonically with distance, the system will favor a maximum thickness d and will thus tend to minimize the interfacial area, hence our proposed interfacial interaction, which is incompatible with the bulk free energy minimized by a close-packed arrangement of micelles. In the following, we compare the free energies of fcc, bcc, and A15 lattices and estimate the strength of the interfacial interaction such that the structure of the micellar crystal is dictated by the minimal-area principle.

The calculation of the bulk free energies of condensed systems is fairly complicated even for hard-sphere systems and the best theoretical results are obtained numerically. It is interesting to note that elaborate analytic models, such as the high-density analog of the virial expansion [15] and the weighted-density-functional approximation [16], are only slightly better than the simple cellular free-volume theory [16,17]. The free-volume theory is a high-density approximation where each micelle is contained in a cell formed by its neighbors, and the communal entropy associated with the correlated motion of micelles is neglected.

Within this theory, the positional entropy of a micelle is determined by the configurational space of its Voronoi or Wigner-Seitz cell. In the fcc lattice, the centers of mass of the micelles are within rhombic dodecahedra [18], while in the bcc lattice they are contained in regular octahedra although the bcc Voronoi cell is an orthic tetrakaidecahedron [18]. For these lattices, the bulk free energy of a micelle is given by

$$F_{\text{bulk}}^{X} = -k_B T \ln\left[\alpha^{X}\left(\frac{\beta^{X}}{n^{1/3}} - 1\right)^3\right], \tag{2}$$

where X is either fcc or bcc, $n = \rho R^3$ is the reduced number density, and R is the hard-core radius of micelles. The coefficients $\alpha^{\text{fcc}} = 2^{5/2}$ and $\alpha^{\text{bcc}} = 2^2 3^{1/2}$ depend on the shape of the cells, whereas $\beta^{\text{fcc}} = 2^{-5/6}$ and $\beta^{\text{bcc}} = 2^{-5/3}3^{1/2}$ are determined by their size.

The A15 lattice is somewhat more complicated: as shown in Fig. 1d the A15 unit cell includes six columnar sites, which make up three perpendicular interlocking columns, and two interstitial sites. A pseudo-Voronoi construction (subject to the constraint that all cells have equal volume) for this lattice leads to a partition consisting of irregular pentagonal dodecahedra and tetrakaidecahedra with two hexagonal and twelve pentagonal faces [19]. Because of the irregularity of the cells, we calculate the bulk entropic free energy numerically, and the result is shown in Fig. 2. For our purposes we require an analytic form: by substituting the dodecahedra and tetrakaiecahedra by spheres and cylinders, respectively, and allowing for two adjustable parameters C and S, which measure the deviation of the Voronoi cells from these spheres and cylinders, we find

$$F_{\text{bulk}}^{\text{A15}} = -k_B T\left\{\frac{1}{4}\ln\left[\frac{4\pi S}{3}\left(\frac{\sqrt{5}}{4n^{1/3}} - 1\right)^3\right] + \frac{3}{4}\ln\left[2\pi C\left(\frac{\sqrt{5}}{4n^{1/3}} - 1\right)^2\left(\frac{1}{2n^{1/3}} - 1\right)\right]\right\}. \tag{3}$$

This form is within 0.1% of the numerical result with $S \approx 1.64$ and $C \approx 1.38$.

The interfacial free energy is minimized by the division of space with smallest area. The problem of finding the partition of space into equal-volume cells with the minimum interfacial area was first studied by Kelvin [20]: he proposed a bcc lattice of orthic tetrakaidecahedra with slightly curved hexagonal faces to satisfy the Plateau rules [12]. However, the Weaire-Phelan partition, which differs from the equal-volume Voronoi construction for the A15 lattice only in a delicate curvature of the pentagonal faces, is 0.3% more efficient [13]. We note that the bcc and A15 structures are among the simplest tetragonal close-packed lattices [21], suggesting that other, more complex close-packed, lattices might be more efficient still. However, the A15 structure appears to be the most efficient, although no proof of its supremacy exists.

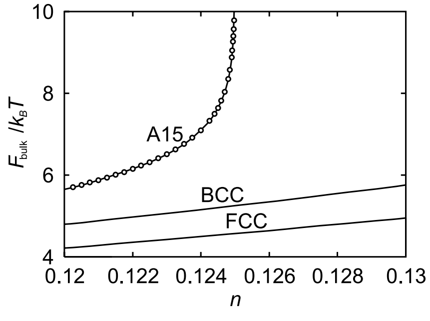

FIG. 2. Bulk free energies of fcc, bcc, and A15 lattice at reduced densities above the melting point. Solid lines: analytical results, Eqs. (2) and (3); circles: numerical results.

To argue that the A15 and bcc lattices are the equilibrium structures formed by micelles, we must estimate the entropy penalty per unit area and translate this into an entropy per dodecyl chain. The dodecyl bilayer is modeled as a polymer brush consisting of chain molecules attached to hard cores, and in the limit of high interdigitation its free energy consists solely of the excluded-volume repulsion of the chains:

$$F_{\text{surf}} = \frac{2\ell N k_B T}{d}, \tag{4}$$

where d is the layer thickness, ℓ is a parameter with the dimension of length, and N is the number of chains per micelle [22]. Since the bilayer must fill the free volume, $A_M d = 2(n^{-1} - 4\pi/3)R^3$, where A_M is the interfacial area per micelle. Thus the interfacial free energy of a micelle is

$$F^x_{\text{surf}} = \frac{\ell N k_B T}{R} \frac{\gamma^x n^{-2/3}}{n^{-1} - 4\pi/3}, \tag{5}$$

where $A_M = \gamma^x V_M^{2/3}$ is the surface area of a cell of volume V_M. For the lattices we consider, $\gamma^{\text{fcc}} = 2^{5/6}3 = 5.345$, $\gamma^{\text{bcc}} = 5.306$, and $\gamma^{\text{A15}} = 5.288$ [23].

We now calculate the range of ℓ such that the total free energy

$$F^x = F^x_{\text{bulk}} + F^x_{\text{surf}} \tag{6}$$

is minimized by the bcc and A15 lattices rather than by the naive, close-packed, fcc lattice. In order to estimate the strength of the soft repulsion, we must first determine the actual reduced density n. Since the hard-core radius of the micelles is unknown, we limit n by recognizing that it must be larger than the melting density, $n \approx 0.120$ for hard spheres [16], and that it must be smaller than the close-packing density of the A15 lattice, $n = 0.125$. The most conservative lower bound of ℓ corresponds to the lowest possible density, i.e., the melting density. With $N = 162$ chains per micelle [1], we find that at $n = 0.120$ the fcc to bcc transition occurs for $\ell \approx 0.1R$ and the bcc to A15 transition occurs for $\ell \approx 0.3R$. This corresponds to an entropy per chain of $0.5k_B$ and $1.5k_B$, respectively. Both values are of the correct order of magnitude and the higher value of the latter is consistent with the relative rarity of the A15 phase.

Since we expect that each chain has at least k_B of entropy, we conclude that the energetics of the dendrimer micelles is dominated by interfacial effects. This is hardly surprising. The number of degrees of freedom of each micelle is quite large and the bulk free energy depends only on the position of the micelle as a whole. Since the micelles are soft, the internal degrees of freedom such as the chain conformations play an important role.

This paradigm, which shows that the minimal surface problem can be fruitfully transplanted to the microscopic level, explains the morphology of a number of dense micellar systems. The same ideas can be applied to polymeric micelles made of, e.g., polystyrene-polyisoprene diblock copolymers dispersed in decane [6,7]. In this case, the micelles are characterized by highly concentrated polystyrene cores and diffuse polyisoprene coronas, and they form bcc or fcc lattices, depending on the relative length of the polystyrene and polyisoprene chains. The bcc lattice is observed in diblock copolymers with similar lengths of core and coronal segments, whereas the fcc lattice occurs whenever the corona is thin compared to core. This is consistent with our model of the impenetrable core which is responsible for the hard part of the repulsion and which favors arrangements with large free volume. In addition, our model suggests that the A15 lattice is the ground state of an asymmetric diblock with an exceptionally large corona or, equivalently, a corona made of very floppy, "entropy-rich" chains. We note that distinguishing between A15 and bcc in powder-averaged diffraction is delicate: the first three bcc reflections [24] are at $\sqrt{2}$, $\sqrt{4}$, and $\sqrt{6}$, while the first *four* A15 reflections are at $\sqrt{2}$, $\sqrt{4}$, $\sqrt{5}$, and $\sqrt{6}$, and thus a careful study would be necessary.

The existence of the A15 lattice in the dendrimer aggregate also may be regarded as an experimental verification of the recent theoretical developments in minimal surfaces and, in particular, Weaire and Phelan's conjecture that this structure solves the Kelvin problem. At this juncture, the presumably ideal A15 structure has not been observed unambiguously on a macroscopic scale in a soap froth [25]. Last but not least, let us note that similar structures have been found in lyotropic materials, e.g., in lipid bilayers in water [26]. In such systems the intermicellar potential also results in an effective interfacial free energy although it is not steric but substance specific and thus transcends the scope of this discussion.

Our model may be further refined by including the effects of the curvature of the brushlike coats, the strain of the coronas into the interstitial regions, and solvent effects. In addition, the dual problem of determining the structure of foams might be amenable to our analysis through the introduction of excluded volume interactions between the bubbles [27].

We hope that this study elucidates the relation between interaction and structure in supramolecular assemblies. By including an additional global contribution to the free energy we provide a rough yet universal quantitative guideline for the design of self-organized soft materials, which can be used for a number of applications such as photonic band-gap materials [28], Bragg switches [29], and porous microreactors [30]. By tuning the ranges of hard and soft repulsion, one should be able to choose among the spectrum of symmetries from the lattice with minimal interfacial area to the lattice with maximal packing fraction and engineer the crystal structure most fitted for a particular application.

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[1] V. S. K. Balagurusamy, G. Ungar, V. Percec, and G. Johansson, J. Am. Chem. Soc. **119**, 1539 (1997).
[2] V. Percec *et al.,* Nature (London) **391**, 161 (1998).

[3] S. D. Hudson, H.-T. Jung, P. Kewsuwan, V. Percec, and W.-D. Cho, Liq. Cryst. **26**, 1493 (1999).
[4] T. Dotera, Phys. Rev. Lett. **82**, 105 (1999).
[5] M. Watzlawek, C. N. Likos, and H. Löwen, Phys. Rev. Lett. **82**, 5289 (1999).
[6] G. A. McConnell, A. P. Gast, J. S. Huang, and S. D. Smith, Phys. Rev. Lett. **71**, 2102 (1993).
[7] G. A. McConnell and A. P. Gast, Phys. Rev. E **54**, 5447 (1996).
[8] S.-C. Mau and D. A. Huse, Phys. Rev. E **59**, 4396 (1999).
[9] M. W. Matsen and F. S. Bates, J. Chem. Phys. **106**, 2436 (1997).
[10] E. Velasco *et al.,* Phys. Rev. Lett. **85**, 122 (2000).
[11] M. Muthukumar, C. K. Ober, and E. L. Thomas, Science **277**, 1225 (1997).
[12] W. Thomson, Philos. Mag. **24**, 503 (1887).
[13] D. Weaire and R. Phelan, Philos. Mag. Lett. **69**, 107 (1994).
[14] T. Cagin, G. Wang, R. Martin, and W. A. Goddard (to be published).
[15] W. G. Rudd, Z. W. Salsburg, A. P. Yu, and F. H. Stillinger, Jr., J. Chem. Phys. **49**, 4857 (1968).
[16] W. A. Curtin and K. Runge, Phys. Rev. A **35**, 4755 (1987).
[17] J. A. Barker, *Lattice Theory of the Liquid State* (Pergamon, Oxford, 1963), pp. 29–33.
[18] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1953), pp. 59–61.
[19] J. Charvolin and J. F. Sadoc, J. Phys. (Paris) **49**, 521 (1988).
[20] *The Kelvin Problem: Foam Structures of Minimal Surface Area,* edited by D. Weaire (Taylor & Francis, London, 1997).
[21] N. Rivier, Philos. Mag. Lett. **69**, 297 (1994).
[22] S. T. Milner, T. A. Witten, and M. E. Cates, Europhys. Lett. **5**, 413 (1988).
[23] γ^{bcc} and γ^{A15} were computed using Surface Evolver, a software package developed by K. Brakke.
[24] *International Tables for Crystallography,* edited by T. Hahn (D. Reidel Publishing Company, Dordrecht, The Netherlands, 1983).
[25] D. Weaire and R. Phelan, Philos. Mag. Lett. **70**, 345 (1994).
[26] P. Mariani, L. Q. Amaral, L. Saturni, and H. Delacroix, J. Phys. II (France) **4**, 1393 (1994).
[27] D. J. Durian, Phys. Rev. Lett. **75**, 4780 (1995).
[28] İ. İ. Tarhan and G. H. Watson, Phys. Rev. Lett. **76**, 315 (1996).
[29] K.-H. Lin *et al.,* Phys. Rev. Lett. **85**, 1770 (2000).
[30] S. A. Jenekhe and X. L. Chen, Science **283**, 372 (1999).