

Entropy-Driven Formation of the Gyroid Cubic Phase

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We show, by computer simulation, that tapered or pear-shaped particles, interacting through purely repulsive interactions, can freely self-assemble to form the three-dimensionally periodic, gyroid cubic phase. The $Ia3d$ gyroid cubic phase is formed by these particles on both compression of an isotropic configuration and expansion of a smectic A bilayer arrangement. For the latter case, it is possible to identify the steps by which the topological transformation from nonintersecting planes to fully interpenetrating, periodic networks takes place.

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Nonspherical particles with purely repulsive interactions are known to form a number of phases intermediate between the isotropic fluid and crystalline solid states. In the 1980s, computer simulations of hard prolate particles [1] confirmed Onsager's classic prediction [2] that particle shape anisotropy can be a sufficient condition to induce the long-range orientational order found in nematic liquid crystals. Subsequently, hard spherocylinders were shown to form a smectic phase [3], while hard oblate particle systems were found to exhibit both discotic nematic [4] and cubatic order [5].

The phase properties of systems with purely steric interactions are important from a statistical mechanical perspective because the potential energy of a steric system is, by definition, constant. Consequently, the Helmholtz free energy $F = U - TS$ in the constant NVT ensemble is controlled by entropy alone and all phase transitions are entropy driven [6]. The concept of ordered phases forming due to entropic effects is counterintuitive, since entropy is generally associated with disorder. Deeper examination of the transitions noted above shows, however, that they occur when, for example, the global system entropy can be enhanced by the sacrifice of some degree of "local" disorder. As well as defining entropy-driven transitions, studies of hard particle systems also closely inform aspects of the experimental behavior of colloidal suspensions.

In this Letter, we extend the range of phases accessible to purely repulsive objects by showing that tapered or pear-shaped particles can freely self-assemble to form the 3D periodic gyroid cubic phase. Because of their complexity and the supramolecular length scales of their periodicities, very few particle-based simulations of cubic phases have

been performed. The most convincing of these is the molecular dynamics (MD) study of glycerolmonoolein molecules organized in a diamond cubic structure by Marrink and Tieleman [7]. Here, however, the cubic arrangement had to be preconstructed and weak constraints imposed to maintain the structure; without these, this system slowly converted into an inverted hexagonal arrangement [8]. Simulation has also been used to probe the rheological properties of the gyroid phase [9]. Here, though, so as to make hydrodynamic behavior accessible, it was necessary to employ a phenomenological Lattice-Boltzmann description which offered no link to the nature of the underlying particles.

The objects considered here are described by the parametric hard Gaussian overlap (PHGO) approximation to Bézier-curve representations of cylindrically symmetric, tapered objects [10]. The PHGO approach makes it possible to simulate these noncentrosymmetric particles as single-site objects, with little computational overhead beyond that required for conventional ellipsoidal Gaussian overlap particles. As a result, multimillion-step simulation runs on 10 000 particle systems are readily achievable.

The underlying tenet of the PHGO model is that a convex object, such as a pear-shaped particle, can locally be well approximated by an ellipsoid, the appropriate ellipsoid being dependant on the direction from which the convex object is viewed. In the PHGO model, this approach is implemented by giving the effective ellipsoid lengths and breadths parametric dependence on the relative positions and orientations of the particles involved. As detailed in Ref. [10] the PHGO contact function for two particles i and j is then expressed as

$$\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = \sigma_0 \left[1 - \chi \left\{ \frac{\alpha^2 (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i)^2 + \alpha^{-2} (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_j) - 2\chi (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i)(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_j)(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)}{1 - \chi^2 (\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)^2} \right\} \right]^{-1/2}, \quad (1)$$

where

$$\sigma_0 = \sqrt{\frac{d_i^2 + d_j^2}{2}}, \quad (2)$$

$$\alpha^2 = \left[\frac{(l_i^2 - d_i^2)(l_j^2 + d_j^2)}{(l_j^2 - d_j^2)(l_i^2 + d_i^2)} \right]^{1/2}, \quad (3)$$

$$\chi = \left[\frac{(l_i^2 - d_i^2)(l_j^2 - d_j^2)}{(l_j^2 + d_j^2)(l_i^2 + d_i^2)} \right]^{1/2}. \quad (4)$$

Here, $\hat{\mathbf{u}}_i$ is the unit orientation vector of particle i and $\hat{\mathbf{r}}_{ij}$ is the interparticle unit vector. l_i and d_i are the instantaneous length and breadth values associated with particle i . For tapered particles, these are effectively expressed as power series expansions in the dot product $(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i)$. Thus,

$$d_i(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i) = d_0 + d_1(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i) + \dots + d_{10}(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i)^{10}, \quad (5)$$

$$l_i(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i) = l_0 + l_1(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_i), \quad (6)$$

the coefficients being set to achieve the desired degree of particle tapering. The degree of tapering is characterized by a single parameter, k_θ , which sets the locations of the Bézier control points that define the chosen particle shape [10]. The equivalent particle cone angle is then given by $\arctan(1/k_\theta)$. In this Letter we show results obtained with particles like that shown in the inset of Fig. 1(b), characterized by the parameter values $k = 3$, $k_\theta = 3.8$.

In a previous study we showed, by Monte Carlo (MC) simulation, that slightly tapered PHGO particles with a length to breadth ratio of $k = 5$ form a bilayer smectic phase between the nematic and crystalline solid states [10]. Subsequent simulations using 1250 shorter ($k = 3$) particles again found conventional liquid crystal phases for particles with either pronounced or mild degrees of taper. However, particles with intermediate tapering angles appeared to form a multidomain curved bilayer state in which the particles developed locally well ordered bilayer patches, these being highly curved and randomly distributed throughout the simulation box.

By extending these simulations to system sizes of ≈ 10000 , we have now found that these moderately tapered particles actually spontaneously self-assemble to form a supramolecular 3D periodic arrangement (Figs. 1). Further analysis of this structure shows it to be the $Ia3d$ gyroid cubic phase. This can be seen from Fig. 1(b), which shows the two interpenetrating networks of channels and triply bonded nodes that characterize this phase. This network image was constructed by performing a cluster analysis based on the locations of the blunt ends of the individual tapered particles shown in Fig. 1(a) and constructing 3D wireframe plots of the two independent networks identified by this analysis. We have obtained this periodic $Ia3d$ structure by both compression of isotropic configurations and expansion from an ordered crystal initial configuration through the intermediate smectic A bilayer phase.

For the system depicted in Figs. 1, the $Ia3d$ phase formed at number density $\rho = 0.336$ on compression of

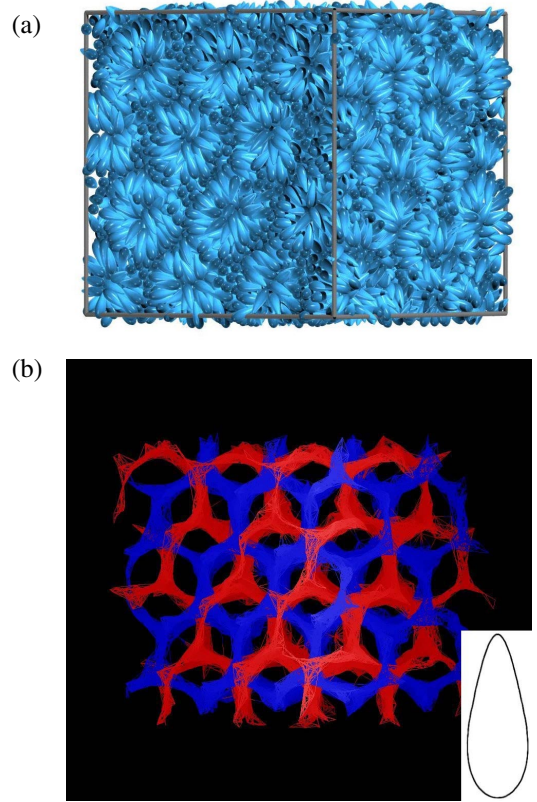


FIG. 1 (color online). (a) Configuration snapshot of an $Ia3d$ structure formed by $k = 3$, $k_\theta = 3.8$ tapered particles. Each tapered particle has a light pointed end and a darker blunt end. (b) Wireframe representation of the two interpenetrating 3D networks [arbitrarily shown in different shades (colors online)] found in the configuration shown in (a) on performing cluster analysis on the blunt ends of the individual tapered particles. Inset: Profile of an individual $k = 3$, $k_\theta = 3.8$ tapered particle.

an isotropic configuration and $\rho = 0.350$ on expansion of a bilayer smectic. The planar smectic bilayer phase could not be regained from compression of the cubic phase, but the isotropic fluid phase *was* readily obtained on expansion of the $Ia3d$ phase. The $Ia3d$ phase shows a reasonably wide range of stability; we have obtained this structure for $k = 3$ particles with $3 \leq k_\theta \leq 4.4$, corresponding to equivalent cone angles of between 12.8° and 18.4° . It is also formed by the $k = 4$, $k_\theta = 4$ system. These structures have been obtained from both MD simulations of a soft-repulsive version of the PHGO model and independent MC simulations of the hard version of the PHGO model. To allow commensurabilities between the $Ia3d$ structure and the simulation box to develop naturally, box-shape variation moves were employed in both sets of simulations to ensure the isotropy of the pressure tensor. The long-time particle mobility determined from the MD simulations was isotropic and of the same order as that obtained in the neighboring smectic A bilayer phase.

The $Ia3d$ structure is well known in experimental studies of lyotropic liquid crystals [11] and block copolymers

and its dividing surface, “the gyroid surface,” is one of the family of infinite periodic minimum surfaces [12]. Supramolecular cubic phases, including the $Ia3d$ structure, have also been seen in studies of thermotropic cubic LC systems [13] based on, e.g., polycatenar [14] and dendrimer [15] molecules. These are solvent-free systems based on highly functionalized molecules comprising flexible and rigid units arranged to promote a variety of molecule shapes (cone, rod and coil, shuttlecock, etc.). Our simulations indicate, though, that particle shape alone is a sufficient condition to induce such behavior.

It is interesting to relate this result to the copolymer and lyotropic systems traditionally associated with the gyroid phase. Generally, the transition from lamellar to gyroid structures is thought to be induced by the interfacial area available becoming large for the total system volume. In traditional gyroid-forming systems, it is relatively straightforward to relate this area to the concentrations and/or chemical compositions of the various components involved. In our repulsive pear systems, the relevant interface is the midsurface of the curved bilayers apparent in Fig. 1(a). The area of this midsurface is itself set by the particle shape and the extent to which the two leaflets interdigitate. The latter is not constrained, however, and has been found to vary with pressure [10]. The gyroid phase usually occupies a narrow region of stability sandwiched between lamellar and hexagonal regions. Like many experimental systems involving tapered (as opposed to wedgelike) dendrimers, however, the repulsive pear-shaped particles studied here do not appear to have a stable hexagonal phase.

Our findings also suggest potential routes towards the self-assembly of 3D periodic structures encompassing a broad range of length scales. Arranging dielectric scatterers on regular arrays is central to work examining photonic band-gap behavior and has motivated studies of self-assembling nanoparticle systems. Our results suggest, however, that appropriate tuning of colloidal particle shape may be sufficient to induce such nanostructures to develop spontaneously. To this end, we note that continuum treatments of vesicle shape predict that pear-shaped objects can spontaneously develop under appropriate conditions [16], while recent work on colloidal particles with protrusions has shown that such objects can be generated reproducibly [17].

We have also used our MD simulations to examine the structural rearrangements associated with the formation of the $Ia3d$ phase on expansion of a bilayer smectic phase to $\rho = 0.350$. The early stages of this are illustrated by the wireframe plots and particle-configuration schematics shown in Figs. 2 and 3, respectively. Figure 2(a) shows a multiple bilayer arrangement adopted within a subregion of our simulation box in the early stages of this run, the four planes indicating the locations of the blunt ends of the individual particles at time step 100 000 [the shade (color online) associated with each particle end at time step 0 is conserved through the image sequence of Fig. 2]. This

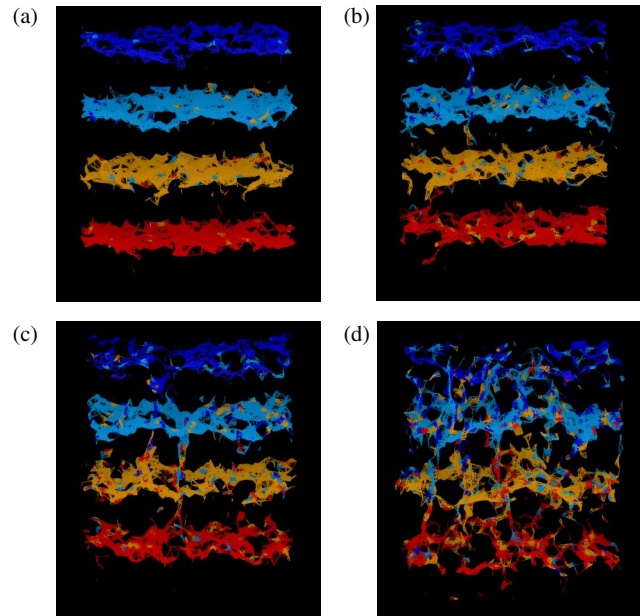


FIG. 2 (color online). Wireframe snapshots depicting the locations of particle blunt ends at various time points following expansion of an initial smectic A bilayer arrangement. These are shown for time steps 100 000 (a), 200 000 (b), 400 000 (c), and 800 000 (d). The original multiplanar topology develops holes (a) through which stalks grow (b),(c) and adapt until the planes become highly fragmented and interconnected (d). Shades (colors online) indicate the planes with which the particle ends were associated at the beginning of the run.

planar topology was maintained for the first 180 000 time steps of the run. Over this time, significant in-plane and a small amount of out-of-plane migration of individual particles was observed. Out-of-plane (or flip-flop) migration is apparent from the occasional spotting of the planes with the shades (colors online) of their neighboring planes. Additionally, multiparticle distortions such as that shown in Fig. 3(a) were seen, involving radially aligned arrangements centered on subclusters of particle blunt ends. The occasional formation of these local clusters, involving particles from *two neighboring* bilayers, proved a crucial step in the development of the cubic arrangement. These distortions led to some regions in the bilayer planes being temporarily denuded of particle blunt ends; these correspond to “holes” in the wireframe planes, such as the one apparent in the second plane down in Fig. 2(a). At time step 200 000 this precursor hole in the second plane was penetrated by a “stalk” linking the two neighboring planes [Fig. 2(b)]. A schematic particle-configuration representation of this structure is shown in Fig. 3(b). From the shade (color online) distribution seen along this initial stalk in Fig. 2(b), it is apparent that its formation involved significant material transfer from the neighbor planes; particles from the holed second plane only make up the very central section of the stalk.

Following this first stalk-formation event, further stalks developed [Fig. 2(c)] and some stalk dissolution events

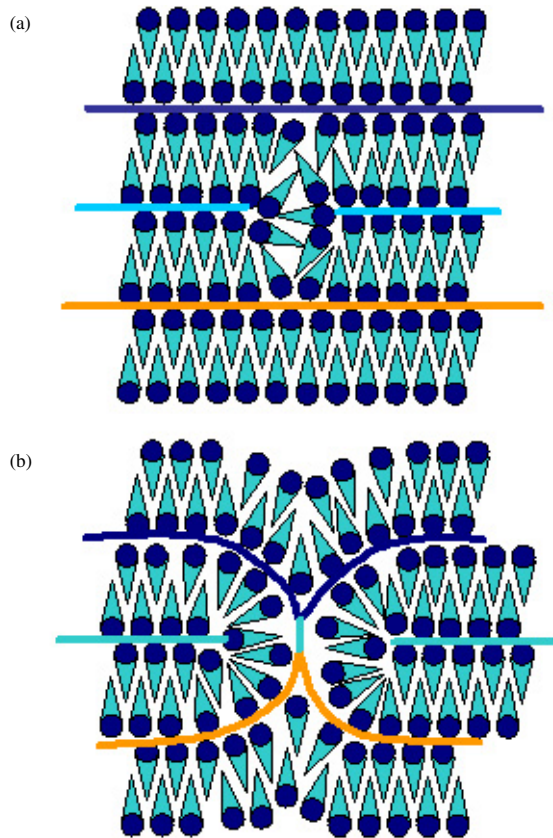


FIG. 3 (color online). 2D particle-resolution schematics showing the configurations adopted to achieve (a) hole formation and (b) stalk formation, corresponding to features apparent from the wireframe snapshots shown in Figs. 2(a) and 2(b), respectively.

also took place. While these processes proved very active, with the stalk arrangements morphing continuously, the instantaneous in-plane distributions of stalks and holes were generally hexagonal, as suggested in a previous experimental assessment of this transition [18]. By time step 800 000 [Fig. 2(d)], the original planar topology was significantly altered, with numerous stalks linking the remnants of the original planes. The considerable mixing of shades (colors online) seen in this figure also indicates the extent of the particle migration exhibited throughout this structural rearrangement. In this simulation, the $Ia3d$ structure of Fig. 1(a) was fully formed by time step 1 500 000, after which it remained essentially unaltered over several million further time steps. While this structure remained fixed, we stress that particle mobility was maintained at its previous level as this simulation was run on. The mechanisms illustrated in Fig. 2 show that each of the two interpenetrating but unconnected networks depicted in Fig. 1(b) was, then, substantially developed from stacks of nonadjacent planes (e.g., planes 1, 3, 5, etc.) in an initial bilayer arrangement. This process was complicated somewhat, by the occasional transfer of particles between leaflets (e.g., by flip-flop) and by the formation of competing domains. However, the underlying mechanism we have

observed here demonstrably follows the scheme proposed 15 yr ago by Clerc *et al.* when considering the topological changes involved in the transitions of their water + surfactant systems [19].

In summary, we have shown, by computer simulation, that hard- and soft-repulsive pear-shaped particles spontaneously form the $Ia3d$ gyroid cubic phase. The ability of these purely repulsive systems to form such a phase represents an extension to the known range of entropy-driven processes. It also raises the prospect that cubic phases may be accessible to suitably shaped aggregates or particles of any size from colloids upwards. By tracking particle configurations, we have also observed the mechanisms by which an initial smectic bilayer arrangement undergoes a topological rearrangement into the gyroid phase.

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