Asymptotic Shape of a Fullerene Ball†

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ABSTRACT

We infer scaling of the shape and energy of a space-enclosing elastic sheet such as a large fullerene ball of linear dimension R. Stretching deformation is crucial in determining the optimal shape, in conjunction with bending. The asymptotic shape of a symmetrical fullerene ball is a flat-sided polyhedron whose edges have an average curvature radius of order $R^{2/3}$. The predicted asymptotic energy is concentrated in these edges and is of order $R^{1/3}$. Analogous edges with this scaling property should occur generally in elastic sheets with discrete disclinations.

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Since the discovery of the spherical C_{60} molecule [1], there is mounting evidence [2,3] for high-molecular-weight "fullerenes"—analogs of C_{60} in which the carbon atoms form a closed, ball-shaped surface. The properties and potential uses of such molecules have aroused great recent interest [2]. In addition, such a surface constitutes a "tethered membrane"; the fluctuations and mechanics of such membranes are of great interest in the statistical physics of complex fluids [4].

When fullerene molecules are sufficiently large, one expects their deformation to be describable using a continuum approach [5], as well as by an atom-by-atom treatment [5,6]. For example, one expects the most symmetrical form of the molecule to be an extended graphite surface, punctuated with twelve five-membered rings so as to form a regular icosahedron with a five-carbon ring at each vertex [2]. Although the network of bonds is that of a flat-sided icosahedron, the shape of the molecule need not be. Instead, the shape relaxes so as to minimize the bond-distortion energy inherent in the structure. Any departure from a flat graphite plane costs distortion energy. To reduce this energy, the

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sharp edges of the icosahedron are expected to soften so that the minimum-energy surface is smooth except near the five-carbon rings. Nearly all of this energy is expected to reside where the bond distortion is weak, *i.e.,* far from the five-membered rings [7]. Thus the energy may be expressed [5,7] in terms of the elastic constants of a weakly deformed graphite membrane.

By adopting such a treatment, we investigate the shape of this smooth surface and its associated elastic energy. We find that the asymptotic shape approaches that of an icosahedron, with nearly-flat faces joined by more strongly curved edges. But the absolute curvature of these edges is weak; the typical edge radius of curvature S increases indefinitely, as a fractional power of the size R. Stretching and bending distortions are responsible for the deformation energy. This energy resides mostly along the edges and should scale as the one-third power of the radius R, as shown below. We first describe how a flat elastic sheet must be distorted to form a closed surface such as a fullerene ball. We recall the energies associated with bending and with stretching and show that stretching must play a leading role in determining the asymptotic shape. Then we construct an energy-balance argument to infer the scaling of the shape and energy with size R. Finally we illustrate this scaling using macroscopic surfaces.

To account for the elastic energy, it is useful to picture the surface as constructed from a continuous material such as paper. In order to form a closed surface, twelve "disclinations" representing the five-fold rings must be introduced. A single disclination may be formed by cutting a sixty-degree sector from a circular sheet of paper and then joining the cut edges. The resulting cone has a local radius of curvature $S(r)$ proportional to the distance from the vertex. The resulting bending energy $B = K \int_s d^2 r S(r)^{-2}$ increases logarithmically with the radius of the cone. Here K is the bending modulus of the surface. Twelve such cones may readily fastened together to form an icosahedron. If the sides of this icosahedron are forced to be flat, the bending energy B resides exclusively at the edges. If these edges have a small radius of curvature S independent of the size R, the total energy is evidently proportional to the total length of the edges, and hence proportional to R.

By relaxing the curvature at the edges, the bending energy may be reduced. However, such softening of the edges is not possible without stretching the material. To see this we assume that the material cannot stretch but can only bend. Then at any given point, curvature is allowed in only one direction; the curvature in the perpendicular direction must be zero. The cones from which our icosahedron was assembled have this property. When the cones are joined together, softening of the edges implies that some of the curvature of the original cones survives in the closed surface. But for points not on the edge, this requires curvature in two independent directions. Such curvature cannot be achieved by pure bending; it requires stretching distortions within the surface. Thus if such stretching is forbidden, only a sharp-edged icosahedron is allowed.

Intuitively, such stretching should be difficult relative to bending for a large, thin surface. Indeed, one may easily verify this on dimensional grounds. Any in-plane distortion such as stretching costs an elastic energy of the form $U \simeq G \int_s d^2 r (du/dr)^2$. Here $u(r)$ is the position of some point on the surface s. The du/dr represents the local strain tensor. (The exact tensor form and the specific elastic constants defining U are not necessary for our argument.) The associated moduli G have dimensions of energy per unit area. If we consider a family of smoothly curved surfaces of identical shape (and strain) but differing in overall size R, the energy U is evidently proportional to R^2. However, the bending energy B defined above is independent of R. Thus the energy cost of any assumed softening of the edges becomes prohibitive as the size R is scaled to infinity. We conclude that any curvature radius S_e at the edges must become arbitrarily small relative to the average curvature $1/R$. Thus the bending energy $B \simeq R/S_e$, must become arbitrarily large relative to that of the cones, and must thus grow faster than the $\mathcal{O}(\log(R))$ energy of the the individual cones.

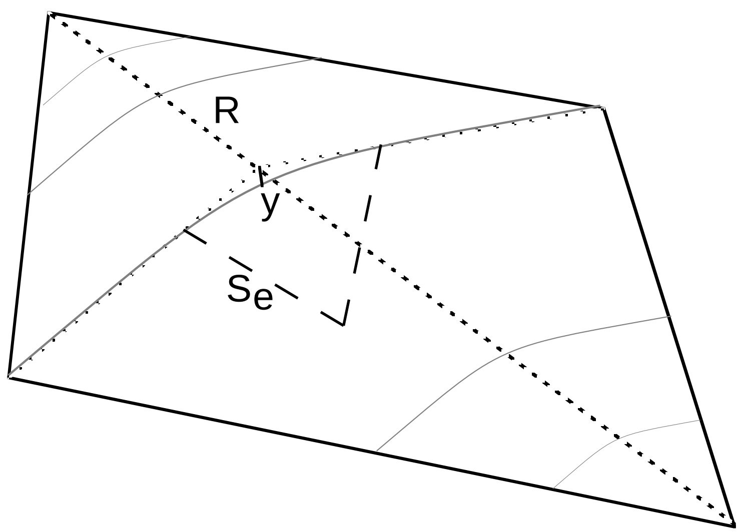

Figure 1. Bending of a diamond-shaped surface. The edge length R, the transverse radius of curvature S_e at the midpoint, and the displacement y of this midpoint from the ridge of a sharply creased surface are shown.

Though S_e must be small relative to R, it may still increase in absolute terms as R increases. To estimate this increase, one must examine the interplay between bending and stretching in more detail. To find the shape via standard methods requires the solution of two coupled, nonlinear partial differential equations for the shape of the surface and the strain field within it [8]. To extract the scaling behavior of the curvature S_e^{-1} from these equations is a subtle task, and we know of no such treatment. However one may educe the scaling of S_e by a simple model. We modify the fullerene surface by fastening rigid bars from the vertices to the center of each face, and forcing the three bars in each face to be coplanar. (The addition of these bars distorts the surface and increases the energy somewhat.) We then consider the diamond-shaped region between the four bars surrounding a given edge. In an exact icosahedron the diamond would be creased along its long diagonal at a 138-degree angle. The other two corners lie at midpoints of the triangular faces. Each such diamond-shaped region may relax from this creased shape in order to reduce the elastic energy, thus forming a continuously curved surface. As argued above, we expect that the dominant curvature lies along the edges of this surface.

One may estimate the elastic energies in terms of the typical S_e. The bending energy B is concentrated in the region within roughly S_e of an edge. Its length is of order R. Thus $B \simeq KR/S_e$; the bending energy resists curvature. But a reduced curvature entails increased stretching of the edge region. The curvature causes the midline of the bend to retract inward relative to the straight polyhedron edge by an amount y of order S_e, as shown in Figure 1. Thus the length of this midline is increased by a factor of roughly $(1 + (S_e/R)^2)^{1/2} \simeq 1 + \mathcal{O}(S_e/R)^2$. Accordingly, the edge region undergoes a stretching strain du/dr of order $(S_e/R)^2$. The associated stretching energy U is of order $GRS_e(du/dr)^2 \simeq GRS_e(S_e/R)^4$ [9]. Hence the ratio $U/B \simeq (G/K)S_e^2(S_e/R)^4$.

The surface chooses that shape and hence that S_e which minimizes $B+U$. Since B and U have power-law dependence on S_e, the two are of comparable size at the optimum $S_e \equiv \tilde{S}(R)$. Since $U/B \sim R^0$, we infer $\tilde{S}(R) \sim R^{2/3}$, so that $B \simeq U \sim R^{1/3}$. This is the result announced above. The model gives an upper bound on the strain energy U. We argue below that further relaxation does not alter U qualitatively.

One may question whether a polyhedral elastic sheet would stretch along its edges like the rigidly held diamond of Figure 1. Instead, one might imagine that as the sheet is allowed to relax from the sharp-edged initial shape, the corners would contract towards each other. Then the straight-line distance between two corners would be reduced and the stretching of the softened edge would be mitigated. But the cost of such a contraction would be greater than its benefit. If the three corners of a face approached each other by fractional amount γ, this would produce a strain of order γ throughout much of the face. The cost of relieving the stretching at the edges would be to create comparable strain throughout the faces. Thus it seems plausible that the contraction of the corners is not important, and that the diamond model is reasonable.

An alternative estimate of the strain energy can be made using the "topological electrostatics" representation of Nelson, valid for weakly deformed flat surfaces [10]. For such surfaces, one may represent the strain energy U in the form $U = G \int d^2 r \gamma^2$. Here G is a particular combination of bulk and shear moduli and $\gamma(r)$ is a particular scalar combination of the strain tensor du/dr. This γ can be expressed as a fictitious electrostatic potential generated by a charge density equal to the gaussian curvature $\bar{C}$: $\nabla^2 \gamma = \bar{C}$. (The Gaussian curvature at a point is the inverse of the product of the two principal radii of curvature.) In the diamond shape of Figure 1, the Gaussian curvature along the edge is of order $-(1/S_e)(y/R^2) \simeq 1/R^2$. This line of negative curvature is flanked by two regions of compensating positive curvature. These regions are at the boundary of the edge region. Interpreting these curvatures as charge densities, one may readily determine the associated potential γ. The "electric field" is equal to the linear charge density $\bar{C} S_e$. The charge separation is of order S_e. Thus the potential $\gamma \simeq \bar{C} S_e^2$. This strain field is present in the edge region, whose area is of order $R S_e$. Combining, we obtain $U \simeq G(R S_e)(S_e/R)^4$, in agreement with the previous estimate.

The progressive flattening of the faces predicted above is illustrated in Figure 2. This photograph shows a triangle of an elastic sheet whose corners have been bent into disclinations. Two triangles differing by a factor of five in size were made from the same sheet of material. The progressive flattening of the face with increasing size is evident from the reduced curvature of the highlight nearest the viewer.

Our prediction may be compared with Tersoff's recent energy calculation for icosahedral fullerenes with 1–36 inequivalent carbon atoms [5]. These energies accurately follow a $\log(R)$ scaling, and they are much less consistent with our predicted $R^{1/3}$ scaling. Thus it seems that even larger molecules than these are required in order to attain the asymptotic regime. Our prediction could also be tested by an explicit calculation for a macroscopic sheet, but we know of no such calculation.

It appears that shapes and energies of large fullerenes have scaling features that had not been anticipated. More broadly, such scaling should describe an arbitrary elastic sheet cut and fastened so as to enclose a region of space. We expect crumpled elastic membranes with discrete disclinations to form edges described by this scaling, as well. It would be valuable to corroborate our

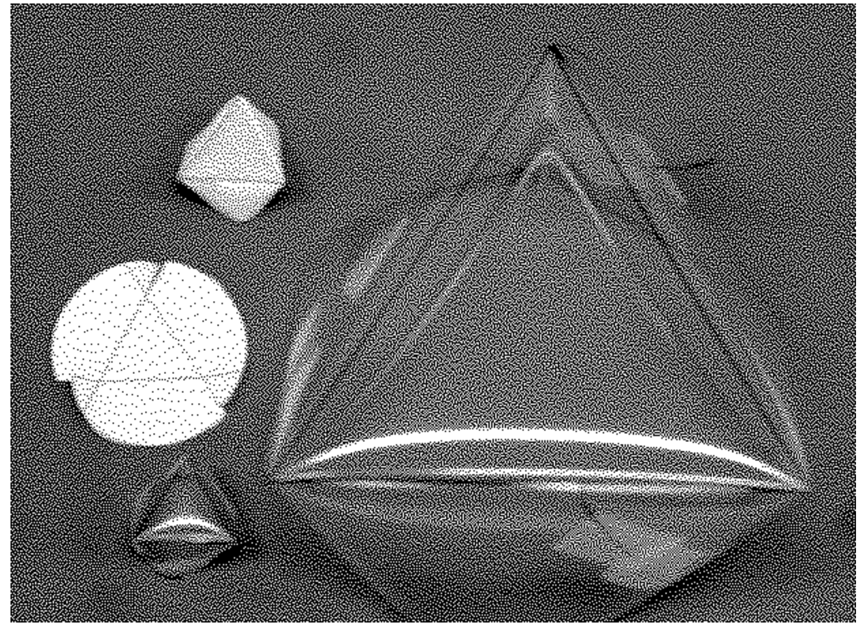

Figure 2. Macroscopic models of a face of a fullerene ball made from a projection transparency sheet as described in the text. Paper copies of the initial sheet and its final bent shape are shown to aid recognition.

scaling arguments with systematic calculations.

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