

Fluctuating shells under pressure

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Edited by T. C. Lubensky, University of Pennsylvania, Philadelphia, PA, and approved October 12, 2012 (received for review July 19, 2012)

Thermal fluctuations strongly modify the large length-scale elastic behavior of cross-linked membranes, giving rise to scale-dependent elastic moduli. Whereas thermal effects in flat membranes are well understood, many natural and artificial microstructures are modeled as thin elastic shells. Shells are distinguished from flat membranes by their nonzero curvature, which provides a size-dependent coupling between the in-plane stretching modes and the out-of-plane undulations. In addition, a shell can support a pressure difference between its interior and its exterior. Little is known about the effect of thermal fluctuations on the elastic properties of shells. Here, we study the statistical mechanics of shape fluctuations in a pressurized spherical shell, using perturbation theory and Monte Carlo computer simulations, explicitly including the effects of curvature and an inward pressure. We predict novel properties of fluctuating thin shells under point indentations and pressure-induced deformations. The contribution due to thermal fluctuations increases with increasing ratio of shell radius to thickness and dominates the response when the product of this ratio and the thermal energy becomes large compared with the bending rigidity of the shell. Thermal effects are enhanced when a large uniform inward pressure acts on the shell and diverge as this pressure approaches the classical buckling transition of the shell. Our results are relevant for the elasticity and osmotic collapse of microcapsules.

The elastic theory of thin plates and shells (1), a subject over a century old, has recently found new applications in understanding the mechanical properties of a wide range of natural and artificial structures at microscopic length scales. The mechanical properties of viral capsids (2–4), red blood cells (5), and hollow polymer and polyelectrolyte capsules (6–10) have been measured and interpreted in terms of elastic constants of the materials making up these thin-walled structures. Theoretically, models that quantify the deformation energy of a 2D membrane have been used to investigate the shapes of viral capsids (11–13) and their expected response to point forces and pressures (14–17), as well as shape transitions of pollen grains (18).

Like its counterparts in other areas of science, such as fluid dynamics and the theory of electrical conduction in metals, thin shell theory aims to describe the physics of slowly varying disturbances in terms of a few macroscopic parameters, such as the shear viscosity of incompressible fluids and the electrical conductivity of metals. Despite such venerable underpinnings as the Navier–Stokes equations and Ohm’s law, these hydrodynamic theories can break down, sometimes in spectacular ways. For example, it is known from mode coupling theory (19) and from renormalization group calculations (20) that thermal fluctuations cause the shear viscosity of incompressible fluids to diverge logarithmically with system size in a 2D incompressible fluid. In the theory of electrical conduction, quenched disorder due to impurities coupled with interactions between electrons lead to a dramatic breakdown of Ohm’s law in thin films and one-dimensional wires at low temperatures, with a conductance that depends on the sample dimensions (21).

Even more dramatic breakdowns of linear response theory can arise in thin plates and shells. Unlike the macroscopic shell structures of interest to civil engineers, thermal fluctuations can strongly influence structures with size of order microns, because the elastic deformation energies of extremely thin membranes (with nanoscale thicknesses) can be of the order of the thermal

energy $k_B T$ (where k_B is the Boltzmann constant and T the temperature) for typical deformations. The statistical mechanics of flat solid plates and membranes (i.e., membranes with no curvature in the unstrained state) have been studied previously (see refs. 22 and 23 and references therein). Thermal fluctuations lead to scale-dependent elastic moduli for flat membranes, causing the in-plane elastic moduli to vanish at large length scales while the bending rigidity diverges (24, 25). These anomalies arise from the nonlinear couplings between out-of-plane deformations (transverse to the plane of the undeformed membrane) and the resultant in-plane strains, which are second order in the out-of-plane displacements.

Much less is known about spherical shells subject to thermal fluctuations (Fig. 1*A*). In fact, the coupling between in-plane and out-of-plane modes is significantly different. Geometry dictates that a closed spherical shell cannot be deformed without stretching; as a result, out-of-plane deformations provide a first-order contribution to the in-plane strain tensor (1). This introduces new nonlinear couplings between in-plane and out-of-plane deformations, which are forbidden by symmetry in flat membranes. We can also consider the buckling of spherical shells under uniform external pressure, which has no simple analog for plates (Fig. 1*B*). An early exploration with computer simulations combined an analysis of the elastic energy due to the linear strain contributions of a spherical membrane with the nonlinear corrections from flat membranes to suggest new scaling behavior for thermally fluctuating spherical membranes (26). However, an important nonlinear coupling triggered by the curved background metric was not considered, nor was the effect of an external pressure investigated. Here, we study the mechanics of fluctuating spherical shells, using perturbation theory and numerical simulations, taking into account the nonlinear couplings introduced by curvature as well as the effects of a uniform external pressure.

Results and Discussion

Elastic Energy of a Thin Shell. The elastic energy of a deformed spherical shell of radius R is calculated using shallow-shell theory (27). This approach considers a shallow section of the shell, small enough so that slopes measured relative to the section base are small (Fig. S1). The in-plane displacements of the shallow section are parameterized by a two-component phonon field $u_i(\mathbf{x})$, $i = 1, 2$; the out-of-plane displacements are described by a field $f(\mathbf{x})$ in a coordinate system $\mathbf{x} = (x_1, x_2)$ tangent to the shell at the origin. We focus on amorphous shells, with uniform elastic properties, and can thus neglect the effect of the 12 inevitable disclinations associated with crystalline order on the surface of a sphere (11). In the presence of an external pressure p acting inward, the elastic energy for small displacements in terms of the

Author contributions: J.P., G.A.V., G.G., and D.R.N. designed research; J.P. and G.A.V. performed research; J.P., G.A.V., G.G., and D.R.N. contributed new reagents/analytic tools; G.A.V. analyzed data; and J.P., G.A.V., G.G., and D.R.N. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1212268109/-DCSupplemental.

bending rigidity κ and Lamé coefficients μ and λ reads (details in *SI Text*)

$$G = \int d^2x \left[\frac{\kappa}{2} (\nabla^2 f)^2 + \mu u_{ij}^2 + \frac{\lambda}{2} u_{kk}^2 - pf \right], \quad [1]$$

where the nonlinear strain tensor is

$$u_{ij}(\mathbf{x}) = \frac{1}{2} (\partial_i u_j + \partial_j u_i + \partial_i f \partial_j f) - \delta_{ij} \frac{f}{R}. \quad [2]$$

Here, $d^2x \equiv \sqrt{g} dx_1 dx_2$, where g is the determinant of the metric tensor associated with the spherical background metric. Within shallow shell theory, $g \approx 1$ (*SI Text*).

If we represent the normal displacements in the form $f(\mathbf{x}) = f_0 + f'(\mathbf{x})$, where f_0 represents the uniform contraction of the sphere in response to the external pressure, and f' is the deformation with reference to this contracted state so that $\int d^2x f' = 0$, then the energy is quadratic in fields u_1, u_2 , and f_0 . These variables can be eliminated in a functional integral of $\exp(-G[f', f_0, u_1, u_2]/k_B T)$ by Gaussian integration (details in *SI Text*). The effective free energy G_{eff} that results is the sum of a harmonic part G_0 and an anharmonic part G_1 in the remaining variable $f'(\mathbf{x})$,

$$G_0 = \frac{1}{2} \int d^2x \left[\kappa (\nabla^2 f')^2 - \frac{pR}{2} |\nabla f'|^2 + \frac{Y}{R^2} f'^2 \right], \quad [3]$$

$$G_1 = \frac{Y}{2} \int d^2x \left[\left(\frac{1}{2} P_{ij}^T \partial_i f' \partial_j f' \right)^2 - \frac{f'}{R} P_{ij}^T \partial_i f' \partial_j f' \right],$$

where $Y = 4\mu(\mu + \lambda)/(2\mu + \lambda)$ is the 2D Young's modulus and $P_{ij}^T = \delta_{ij} - \partial_i \partial_j / \nabla^2$ is the transverse projection operator. The “mass” term $Y(f'/R)^2$ in the harmonic energy functional reflects the coupling between out-of-plane deformation and in-plane stretching due to curvature, absent in the harmonic theory of flat membranes (plates). The cubic interaction term with a coupling constant $-Y/2R$ is also unique to curved membranes and is prohibited by symmetry for flat membranes. These terms are unusual because they have system-size-dependent coupling constants. Note that an inward pressure ($p > 0$) acts like a negative R -dependent surface tension in the harmonic term. As required, the effective elastic energy of fluctuating flat membranes is retrieved for $R \rightarrow \infty$ and $p = 0$. In the following, we exclusively use the field $f'(\mathbf{x})$ and thus drop the prime without ambiguity.

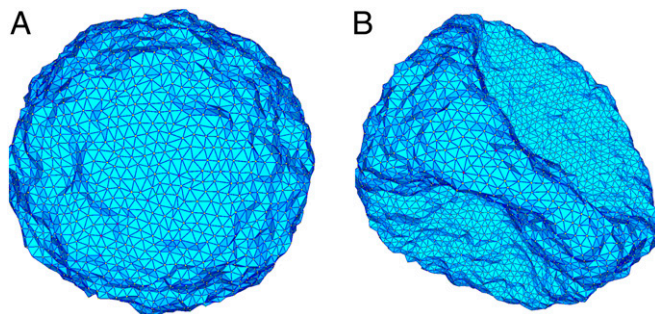


Fig. 1. Simulated thermally fluctuating shells. (A) Triangulated shell with 5,530 points separated by average nearest-neighbor distance r_0 with Young's modulus $Y = 577\epsilon/r_0^2$ and bending rigidity $\kappa = 50\epsilon$ at temperature $k_B T = 20\epsilon$, where ϵ is the energy scale of the Lennard-Jones potential used to generate the disordered mesh. (B) Same as in A with external pressure $p = 0.5p_c$, where p_c is the classical buckling pressure. The thermally excited shell has already buckled under pressure to a shape with a much smaller enclosed volume than in A.

When only the harmonic contributions are considered, the equipartition result for the thermally generated Fourier components $f_{\mathbf{q}} = \int d^2x f(\mathbf{x}) \exp(i\mathbf{q} \cdot \mathbf{x})$ with 2D wavevector \mathbf{q} are

$$\langle f_{\mathbf{q}} f_{\mathbf{q}'} \rangle_0 = \frac{Ak_B T \delta_{\mathbf{q}, -\mathbf{q}'}}{\kappa q^4 - \frac{pR}{2} q^2 + \frac{Y}{R^2}}, \quad [4]$$

where A is the area of integration in the (x_1, x_2) plane. Long-wavelength modes are restricted by the finite size of the sphere; i.e., $q \gtrsim 1/R$. In contrast to flat membranes for which the amplitude of long-wavelength ($q \rightarrow 0$) modes diverges as $k_B T / (\kappa q^4)$, the coupling between in-plane and out-of-plane deformations of curved membranes cuts off fluctuations with wave vectors smaller than a characteristic inverse length scale (26),

$$q^* = (\ell^*)^{-1} = \left(\frac{Y}{\kappa R^2} \right)^{1/4} \equiv \frac{\gamma^{1/4}}{R},$$

where we have introduced the dimensionless Föppl-von Kármán number $\gamma = YR^2/\kappa$ (11). We focus here on the case $\gamma \gg 1$, so $\ell^* \ll R$. As p approaches $p_c \equiv 4\sqrt{\kappa Y}/R^2$, the modes with $q = q^*$ become unstable and their amplitude diverges. This corresponds to the well-known buckling transition of spherical shells under external pressure (27). When $p > p_c$, the shape of the deformed shell is no longer described by small deformations from a sphere, and the shallow shell approximation breaks down.

Anharmonic Corrections to Elastic Moduli. The anharmonic part of the elastic energy, neglected in the analysis described above, modifies the fluctuation spectrum by coupling Fourier modes at different wave vectors. Upon rescaling all lengths by ℓ^* , it can be shown that the size of anharmonic contributions to $\langle |f_{\mathbf{q}}|^2 \rangle$ is set by the dimensionless quantities $k_B T \sqrt{\gamma}/\kappa$ and p/p_c . The correlation function including the anharmonic terms in Eq. 3 is given by the Dyson equation,

$$\langle |f_{\mathbf{q}}|^2 \rangle = \frac{1}{\langle |f_{\mathbf{q}}|^2 \rangle_0^{-1} - \Sigma(\mathbf{q})}, \quad [5]$$

where $\Sigma(\mathbf{q})$ is the self-energy, which we evaluate to one-loop order, using perturbation theory. Whereas $\langle |f_{\mathbf{q}}|^2 \rangle$ can be numerically evaluated at any \mathbf{q} , an approximate but concise description of the fluctuation spectrum is obtained by expanding the self-energy up to order q^4 and defining renormalized values Y_R , κ_R , and p_R of the Young's modulus, bending rigidity, and pressure, from the coefficients of the expansion:

$$Ak_B T \langle |f_{\mathbf{q} \rightarrow 0}|^2 \rangle^{-1} \equiv \kappa_R q^4 - \frac{p_R R}{2} q^2 + \frac{Y_R}{R^2} + O(q^6). \quad [6]$$

To lowest order in $k_B T/\kappa$ and p/p_c we obtain the approximate expressions (details in *SI Text*)

$$Y_R \approx Y \left[1 - \frac{3}{256} \frac{k_B T}{\kappa} \sqrt{\gamma} \left(1 + \frac{4p}{\pi p_c} \right) \right], \quad [7]$$

$$p_R \approx p + \frac{1}{24\pi} \frac{k_B T}{\kappa} p_c \sqrt{\gamma} \left(1 + \frac{63\pi p}{128 p_c} \right), \quad [8]$$

and

$$\kappa_R \approx \kappa \left[1 + \frac{61}{4,096} \frac{k_B T}{\kappa} \sqrt{\gamma} \left(1 - \frac{1,568 p}{915\pi p_c} \right) \right]. \quad [9]$$

RBC membranes correspond to $Y \approx 25 \mu\text{N/m}$ (5, 31), whereas reported values of the bending rigidity κ vary widely from $6 k_B T$ to $40 k_B T$ (5, 32). Using an effective radius of curvature $R \approx 7 \mu\text{m}$ (5) gives $k_B T \sqrt{\gamma}/\kappa$ in the range 2–35. Thus, RBCs could be good candidates to observe our predicted thermal effects, provided their bending rigidity is in the lower range of the reported values.

For continuum shells fabricated from an elastic material with a 3D Young's modulus E , thickness h , and typical Poisson ratio ≈ 0.3 , $k_B T \sqrt{\gamma}/\kappa \approx 100 R k_B T / (E h^4)$. Hence very thin shells with a sufficiently high radius-to-thickness ratio (R/h) must display significant thermal effects. Polyelectrolyte (9) and protein-based (33) shells with $R/h \approx 10^3$ have been fabricated, but typical solid shells have a bending rigidity κ several orders of magnitude higher than $k_B T$ unless $h \leq 5 \text{ nm}$. Microcapsules of 6 nm thickness fabricated from reconstituted spider silk (33) with $R \approx 30 \mu\text{m}$ and $E \approx 1 \text{ GPa}$ have $k_B T \sqrt{\gamma}/\kappa \approx 3$ and could exhibit measurable anharmonic effects.

Thermal effects are particularly pronounced under finite external pressure—an indentation experiment carried out at $p = p_c/2$ on the aforementioned spider silk capsules would show corrections of 10% from the classical zero-temperature theory. For similar capsules with half the thickness, perturbative corrections at $p = p_c/2$ are larger than 100%, reflecting a drastic breakdown of shell theory because of thermal fluctuations. The breakdown of classical shell theory explored here points to the need for a renormalization analysis, similar to that carried out already for flat plates (34).

Materials and Methods

Monte Carlo Simulations of Randomly Triangulated Shells. A random triangulation of radius R_0 is constructed by distributing N nodes on the surface of a sphere with the required radius. The first two of these nodes are fixed at the north and the south pole of the sphere whereas the positions of the remaining $N - 2$ nodes are randomized and equilibrated in a Monte Carlo simulation. During this equilibration process the nodes interact via a steeply repulsive potential (the repulsive part of a Lennard-Jones potential). After equilibration, when the energy has reached a constant value on average, the simulation is stopped and the final configuration is “frozen.” The neighbors of all nodes are determined using a Delaunay triangulation (35). The spherical configurations as well as the connection lists are used in further simulations.

In subsequent simulations nearest neighbors are permanently linked by a harmonic potential giving rise to a total stretching energy (36),

$$E_s = \frac{k}{2} \sum_{ij} (r_{ij} - r_{ij}^0)^2, \quad [14]$$

where the sum runs over all pairs of nearest neighbors, r_{ij} is the distance between two neighbors, and r_{ij}^0 is the equilibrium length of a spring. The equilibrium length r_{ij}^0 is determined at the start of the simulation, when the shell is still perfectly spherical and thus the stretching energy vanishes for the spherical shape. The spring constant k is related to the 2D Lamé coefficients $\lambda = \mu = \sqrt{3}k/4$ and the 2D Young's modulus $Y = 2k/\sqrt{3}$ (36).

The mean curvature (more precisely, twice the mean curvature) at node i is discretized using (30, 37, 38)

$$H_i = \frac{1}{\sigma_i} n_i \cdot \sum_{j(i)} \frac{\sigma_{ij}}{l_{ij}} (r_i - r_j), \quad [15]$$

where n_i is the surface (unit) normal at node i (the average normal of the faces surrounding node i), $\sigma_i = \sum_{j(i)} \sigma_{ij} l_{ij}$ is the area of the dual cell of node i , $\sigma_{ij} = l_{ij} [\cot \theta_1 + \cot \theta_2]/2$ is the length of a bond in the dual lattice, and $l_{ij} = |r_i - r_j|$ is the distance between the nodes i and j . The total curvature energy is

$$E_b = \frac{\kappa}{2} \sum_i \sigma_i (H_i - H_0)^2 \quad [16]$$

with κ the bending rigidity and H_0 the spontaneous curvature at node i . In all

simulations $H_0 = 2/R_0$ (because H_i is twice the mean curvature). In the cases of elastic shells under pressure a term PV is added to the Hamiltonian, where P is the external pressure and V the volume of the shell.

Similar elastic networks with stretching and bending potentials have been studied in relation to the stability of membranes and to icosahedral and spherical shells that contain defects (11, 17, 29, 36, 39, 40) or defect scars (38, 41–43) as well as to the deformation of icosahedral viruses (14–16) and the crumpling of elastic sheets (28).

Simulations are performed for shells of 5,530 ($R_0 = 20 r_0$), 22,117 ($R_0 = 40 r_0$), and 41,816 ($R_0 = 55 r_0$) nodes. The Hookean spring constant and the bending rigidity are taken such that the shells have Föppl-von Kármán numbers in the range $650 < \gamma < 35,000$ and that the dimensionless temperature is in the range $2 \times 10^{-6} < k_B T/\kappa < 0.5$. Monte Carlo production runs consist typically of 1.25×10^8 Monte Carlo steps, where in a single Monte Carlo step an attempt is made to update the positions of all nodes once on average. Configurations were stored for analysis typically every $N_{\text{samp}} = 2,000$ Monte Carlo steps. For the largest system (41,816 nodes), such a run took about 700 d of net central processing unit (CPU) time spread over several simultaneous runs in a Linux cluster of Intel XEON X5355 CPUs. For the smaller shells, the computational time scaled down roughly linearly with system size.

Fluctuation Spectrum from Computer Simulations. For a particular configuration of a simulated shell, the coefficients A_{lm} of the expansion of the radial displacements in spherical harmonics (Eq. 10) are determined by a least-squares fit of the node positions to a finite number l_m of (real) spherical harmonics. In practice we have used $l_m = 26$ as the upper wave-number cutoff for all simulations. At each temperature and pressure, this procedure is repeated for about 10,000 independent configurations and the results are averaged to obtain the curves presented in Fig. 2.

Simulations of Shells Indented by Point-Like Forces. To perform indentation simulations, two harmonic springs are attached to the north and the south pole of the shell. This leads to an additional term in the Hamiltonian $V_s = k_i(z_i^N - z^N)^2/2 + k_i(z_i^S - z^S)^2/2$, where $k_i = \kappa/r_0^2$ is the spring constant of the indenter. Here, one end of the springs, at positions z^N and z^S , is attached to the vertices at the north and the south pole, respectively. The positions of the other end of the springs, at z_i^N and z_i^S , are fixed externally and determine the indentation force and depth, as indicated in Fig. S4.

By changing z_i^N and z_i^S , the depth of the indentation can be varied. After the springs are fixed a certain distance apart, the thermally averaged pole-to-pole distance (z) is measured and compared with its value in the absence of a force, $\langle z_0 \rangle$. The instantaneous force at the poles is calculated from the instantaneous extension of the harmonic springs after each N_{samp} Monte Carlo step; thermal averaging then determines the average corresponding to $\langle z \rangle$. This provides the force-indentation curves in Fig. 3 A and B.

It is very difficult to unambiguously identify the linear regime in the force-indentation curves. Extracting the effective spring constant of shell deformation k_s from a linear fit in the small indentation region is subject to inaccuracies and sensitivity to the number of points included in fitting. Instead, we extract the spring constants of thermally fluctuating shells by using a relation between k_s and the fluctuations in z_0 (derivation in SI Text):

$$k_s \approx \frac{k_B T}{\langle z_0^2 \rangle - \langle z_0 \rangle^2}. \quad [17]$$

This procedure was used to measure the temperature-dependent spring constants in Fig. 3C.

ACKNOWLEDGMENTS. We thank J. Hutchinson and F. Spaepen for pointing us to relevant shell theory literature, and A. Kosmrlj and Z. Zeravcic for useful discussions about theory and simulation details, respectively. Work by J.P. and D.R.N. was supported by the National Science Foundation via Grant DMR1005289 and through the Harvard Materials Research Science and Engineering Center through Grant DMR0820484.

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