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Metastability of a circular o-ring due to intrinsic curvature

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Abstract. An o-ring takes spontaneously the shape of a chair when strong enough torsion is applied in its tangent plane. This state is metastable, since work has to be done on the o-ring to return to the circular shape. We show that this metastable state exists in a Hamiltonian where curvature and torsion are coupled *via* an intrinsic curvature term. If the o-ring is constrained to be planar (2d case), this metastable state displays a kink-anti-kink pair. This state is metastable if the ratio $\alpha = C/A$ is less than $\alpha_c(2\mathrm{d}) = 0.66$, where C and A are the torsion and the bending elastic constants [1]. In three dimensions, our variational approach shows that $\alpha_c(3\mathrm{d}) \simeq 0.9$. This model can be generalized to the case where the bend is induced by a concentration field which follows the variations of the curvature.

PACS. 05.90.+m Other topics in statistical physics and thermodynamics – 03.40.-t Classical mechanics of continuous media: general mathematical aspects – 62.20.Dc Elasticity of solids

Consider a closed toroidal o-ring: Apply a torque at one point while holding the opposite point fixed (see Fig. 1). For small deformations, the shape of the o-ring relaxes to its circular shape after the constraints are removed. However, if the applied torque is larger than a threshold, the o-ring takes spontaneously the shape of a chair. This state is metastable, since no external torque is required. Drawing a line with liquid paper on the o-ring shows that torsion and curvature are unequally distributed along the rod, since torsion is mainly concentrated on the two helical parts of the metastable state. This is reminiscent of the Euler instability [1] for a straight rod, but we show in this paper that this metastable state exists for a circular o-ring where curvature and torsion are locally coupled by an intrinsic curvature term. The parameter of the model is the ratio $\alpha = C/A$, where C and A are the torsion and bending elastic constants. For zero linking number [9], we demonstrate that the critical value α_c below which the chair shape exists depends on the dimension of the space where the o-ring is confined. In a two-dimensional geometry, we find $\alpha_c(2\mathrm{d}) \simeq 0.66$. In the non-planar case (3d), our variational approach shows that $\alpha_c(3\mathrm{d}) \simeq 0.9$.

These values are experimentally accessible with biopolymers materials such as D.N.A. minicircles which are permanently bend for sequence dependent molecules [2–4]. In this case, the salt concentration of the solution controls the bending elastic constant so that α can be decreased below its salt physiological value ($\alpha = 1.5$). To deal with situations where the bend is induced by small particles, we generalize the o-ring model and we show that the local density follows the variations the curvature. Our model is motivated by recent experiments on D.N.A. minicircles where conformational changes are induced by histone like proteins [5].

Such a metastable state is not observed if the o-ring is not intrinsically circular, as for a rubber whose two ends are glued together. The physical origin of this metastable state is traced back to the existence of a threshold value for the torsion applied from outside. Associated with this threshold, there is a broken symmetry due to the intrinsic curvature c_0 of the rod. In the local frame $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ embedded into matter, we write the energy as [2,6–8]

$$H = \frac{1}{2}A \oint \mathrm{d}s \left((\Omega_1 - c_0)^2 + \Omega_2^2 \right) + \frac{1}{2}C \oint \mathrm{d}s\, \Omega_3^2 \quad (1)$$

where $\boldsymbol{\Omega} = (\Omega_1, \Omega_2, \Omega_3)$ is the rate of deformation [1] and s is the arclength. By definition, $\mathbf{e}_3$ is directed along the tangent of the central fibre of the rod whose geometric properties are described by the Serret-Frenet triad $(\mathbf{t}, \mathbf{n}, \mathbf{b})$. Equation (1) accounts for curvature, $\kappa^2 = \Omega_1^2 + \Omega_2^2$, and torsion, Ω_3^2 [1]. It also has a symmetry breaking term $\Omega_1 c_0$. By definition, ψ is the angle that makes $\mathbf{e}_1$ with the osculating plane (see Fig. 1). Writing $c_0\Omega_1 = c_0\kappa \cos\psi$ shows that curvature and torsion are locally coupled. Hereafter, we take $c_0 = R_0^{-1}$, where R_0 is the radius of the undistorted o-ring. The ratio $\alpha = C/A$ is independent of the aspect ratio of the o-ring [1] ($\alpha = 0.66$ for rubber).

The existence of the metastable state can be understood by noticing that the physical triad experiences a rotation of almost $\pm 2\pi$ in each helical arcs. Since the curvature is of the order of c_0 in the two opposite circular

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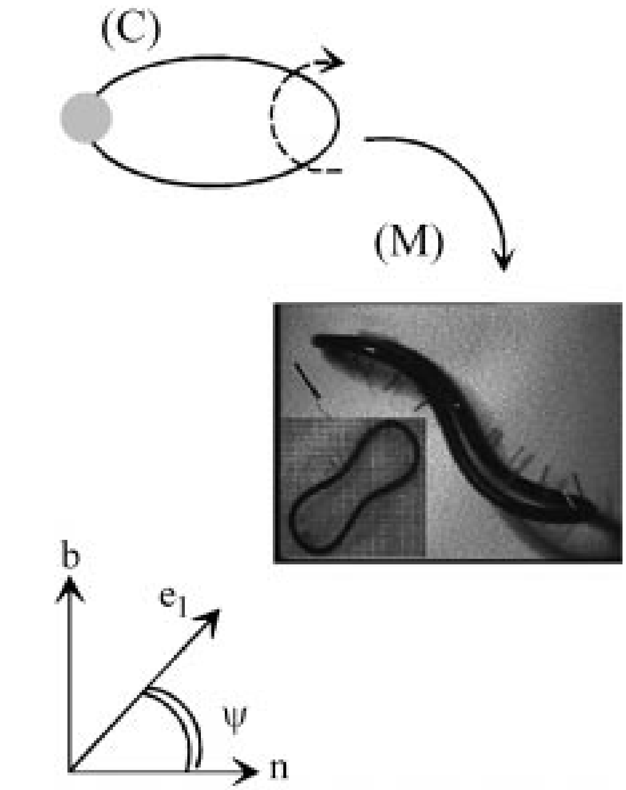

Fig. 1. Case (C): The o-ring is circular. A torque is applied perpendicularly to the neutral fibre as indicated by the arrow and zero torsion is imposed at the opposite point (shaded sphere). If the torsion angle is sufficiently large, the o-ring relaxes to the metastable state. The picture corresponding to the case (M) is a side photograph of an o-ring in the metastable state where the nails indicate how torsion is distributed along the rod. The inset shows the top view of the metastable state. By definition, $\mathbf{t}, \mathbf{b}, \mathbf{n}$ are the tangent, the binormal and the normal to the neutral fibre. The physical triad $(\mathbf{e_1}, \mathbf{e_2}, \mathbf{e_3})$ is embedded into matter.

arcs closing the o-ring, untwisting the helices increases the curvature energy at the two circular ends. Obviously, the energy of the metastable state increases with the ratio $\alpha = C/A$ for a given radius R_0, so that there is a threshold for α above which the metastable state disappears.

First, consider the 2d case, where the binormal $\mathbf{b}$ is parallel to the Z axis. We choose a reference frame X, Y such that the south and north poles of the o-ring in the untwisted state are at $(0, \pm R_0)$, respectively. If the tangent makes an angle ϕ with respect to the X axis, the curvature is $\dot{\phi} = \mathrm{d}\phi/\mathrm{d}s$. Equation (1) is rewritten as

$$H = \frac{1}{2} A \oint \mathrm{d}s \left(\dot{\phi} - c_0\right)^2 + \frac{1}{2} \alpha A \oint \mathrm{d}s\, \dot{\psi}^2 + A c_0 \oint \mathrm{d}s\, \dot{\phi}\, (1 - \cos\psi) \quad (2)$$

where ψ is the angle between $\mathbf{e}_1$ and the (X, Y) plane. The last term in equation (2) couples torsion, ψ, to curvature, $\dot{\phi}$. It shows that the actual intrinsic curvature varies

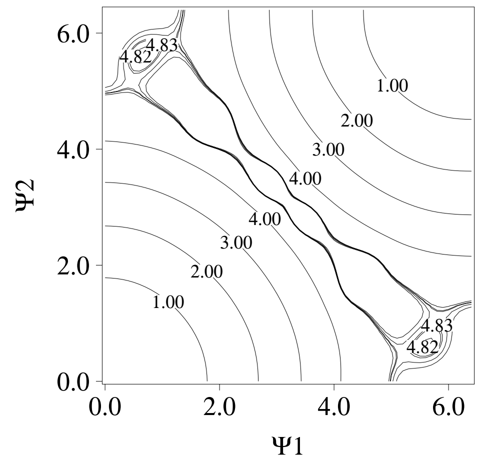

Fig. 2. Energy contour map of the o-ring for different values of the torsion angles $\psi_{1,2}$ imposed at the south and north poles, respectively. This figure corresponds to the planar o-ring (2d case). The circular o-ring has $\psi_2 = \psi_1 = 0$. The metastable state corresponds to the two energy wells along the line $\psi_2 = 2\pi - \psi_1$ ($\alpha = 0.5$).

as $c_0 \cos\psi$. Obviously, $\psi = 0, 2\pi$ are two physically indiscernible minimum energy solutions for the bending energy. In the small $\alpha \ll 1$ limit, we demonstrate that $\psi(s)$ for the metastable solution interpolates between these two values (zero applied torque). However, as α increases, the jump $\Delta\psi$ experienced by ψ between the two circular arcs, where ψ is almost constant, becomes smaller.

To obtain stationary solutions with circular constraints, we add to the equation (2) two Lagrange multipliers

$$\int \mathrm{d}s \lambda(s)(\mathrm{d}x/\mathrm{d}s - \cos\phi) + \int \mathrm{d}s \eta(s)(\mathrm{d}y/\mathrm{d}s - \sin\phi),$$

so that x, y, ϕ have independent variations. Rescaling the arclength by R_0, stationary contours symmetric with respect to the $X = 0$ plane ($\eta = 0$) are solutions of the Euler equations

$$\frac{\mathrm{d}}{\mathrm{d}s}\left[\dot{\phi} - \cos\psi\right] = \lambda \sin\phi$$
$$\xi_0^2 \frac{\mathrm{d}^2\psi}{\mathrm{d}s^2} = \dot{\phi} \sin\psi \quad (3)$$

where the Euler equation for $\lambda(s)$ shows that it is constant. By dimensional analysis, $\xi_0 = \alpha^{1/2} R_0$ is a *persistence length* for torsional deformations. For constant curvature, $\ddot{\phi} = 0$, the torsion's profile induced by an external torque is exponential like and, therefore, short range. This contrasts with the $c_0 = 0$ case, where the profile is linear, indicating thereby a long range perturbation. For the o-ring, ξ_0 set the width of the kink.

Figure 2 shows a three-dimensional contour plot of the energy as a function of the two angles $\psi_{1,2}$ imposed at the north and south pole by an outside torque ($\alpha = 0.5$). For the boundary conditions we consider here, this plot is symmetric with respect to the lines $\psi_2 = \psi_1$ and $\psi_2 = 2\pi - \psi_1$, where $\psi_{1,2}$ are the angle between $\mathbf{e_1}$ and the tangent plane for $X = 0$.

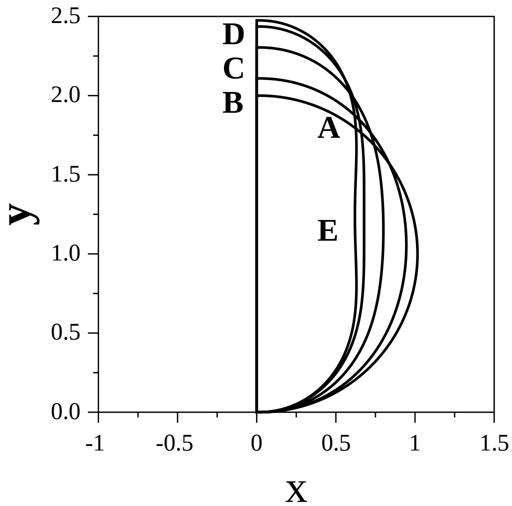

Fig. 3. Shape of half of the o-ring for different values of $\psi_1 = 2\pi - \psi_2$. All shapes are drawn for the same value of the parameter $\alpha = 0.5$. For cases A (circular o-ring), B, C, D, E, one has: $\psi_1 = 3.140, 2.35, 1.57, 0.78, 0$. For $\alpha = 0.5$, the metastable state (zero applied torque) is indistinguishable from case E.

Two cases are interesting:

1) If $\lambda = 0$, solutions of equation (3) are symmetric with respect to the $Y = 0$ axis. This corresponds to the line $\psi_2 = 2\pi - \psi_1$ in the energy diagram of Figure 2. Moving on this line amounts to applying two opposite torques to the o-ring. The metastable state corresponds to the two non-trivial local minima of the energy with zero applied torque $\partial E/\partial\psi_{1,2} = 0$. The actual shape of the o-ring depends on the parameter α as shown in Figure 3 for different cases.

2) Beside the $\lambda = 0$ line, we find solutions which break the symmetry with respect to the $Y = 0$ axis. In all cases, $\dot{\psi}$ is discontinuous at the poles because of the torques applied from outside.

Energy diagrams, such as Figure 2, depend on the value of α. For $\alpha \leq \alpha_c \simeq 0.66$, we find two symmetric local minima along the $\lambda = 0$ line. Moving away from these two points increases the energy and work has to be done on the system to go back to the untwisted state $\psi_{1,2} = 0$. Solutions of the Euler equations make H stationary with respect to all variations with the same boundary conditions. For $\psi_1 = 2\pi - \psi_2$, we find that there exists always a local minimum on the $\lambda = 0$ line which moves from $\psi_1 = 0$ for $\alpha = 0$ to $\psi_1 = \psi_2 = \pi$ when $\alpha = 1$. However, for values of $\alpha > \alpha_c(2\mathrm{d})$, moving perpendicularly off the $\lambda = 0$ line decreases the energy, so that a torque must be applied from outside for the state to be stable. This state is therefore a saddle point solution in the strong torsion regime.

In the symmetric case, $\lambda = 0$, we can study analytically how the metastable state depends on the parameter α. The change of variable $y = \cos\psi$ reduces the shape equations to the standard form

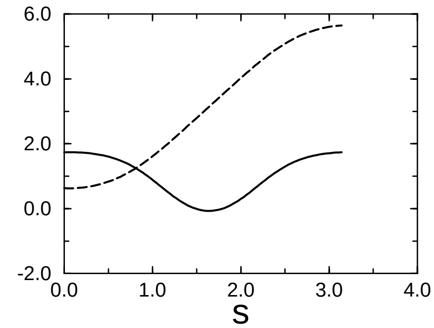

Fig. 4. Variations of the curvature $\dot{\phi}$ (solid line) and of the torsion angle ψ (long dashed line) for the metastable state (2d case, half o-ring).

$$\dot{y}^2 = -V(y)$$
$$\text{with} \quad V(y) = -\xi_0^{-2}\left(y^2 - 1\right)(y-a)(y-b) \tag{4}$$

where a and b are two constants ($b = \cos\psi_{1,2}$). Equation (4) describes the motion of a particle in a potential well $V(y)$ with solutions varying between the zeros of $V(y)$. After Davis [10], the solution is given by an elliptic function

$$y = \cos\psi = \frac{F(u) - b\dfrac{a-1}{a-b}}{F(u) - \dfrac{a-1}{a-b}};$$
$$F(u) = \frac{1}{k^2}\mathrm{sn}^2\left(km\frac{s}{\xi_0}, \frac{1}{k^2}\right) \tag{5}$$

with $k = \left(2\frac{a-b}{a-1}\frac{1}{b+1}\right)^{1/2} > 1$ and $m = \frac{1}{2}\left[(1+b)(1-a)\right]^{1/2}$.

The set (k, m), or equivalently (a, b), is determined by the periodic boundary conditions. Since $\mathrm{sn}^2\left(x, k^{-2}\right)$ is periodic with period $2K[k^{-2}]$, the condition for ψ to be periodic is

$$\pi\frac{km}{K[k^{-2}]} = 2\xi_0 \tag{6}$$

where $K(k^{-2})$ is the modulus of the elliptic function. Since ϕ is also periodic, with $\dot{\phi} = -\frac{1}{2}(a+b) + \cos\psi$, the condition $\phi(2\pi R_0) = \phi(0) + 2\pi$ together with equation (6) yields the two constants a and b. The analytic solution is worthwile to discuss in the two limiting cases of small and large α regime.

1) In the small α limit, $\xi_0 \ll 1$, the variations of the torsion angle ψ are large, since the restoring force is small. In this case, $b = 1^-$ and ψ experiences rapid variations between its two limiting values which are almost 0 and 2π. Since $k \to 1^+$, we have $K(1/k^2) \to \infty$ with $m \simeq 1$, and the elliptic function is well approximated by a hyperbolic tangent. The mechanical analog is a particle oscillating in a double well potential at $\psi = 0^+$ and $\psi = 2\pi^-$. Figure 4 shows the variations of the curvature, $\dot{\phi}$, and of the torsion, ψ, as a function of the arclength. A well-defined plateau

separates the kink-anti-kink where the torsion experiences a tanh-like variation.

2) In the large α regime, the elliptic function is well approximated by a sinusoid and the domain walls cannot be distinguished. The limiting case $b = \cos\psi_{1,2} = -1$ corresponds to the unstable solution where the o-ring experiences a global torsion of π ($\alpha = 1$). In practice the metastable state disappears much before the strong torsion regime.

Let us consider the 3d case. The deformation rate along the tangent of the curve depends on the geometric torsion of the neutral fibre τ_g as $\Omega_3 = \dot{\psi} + \tau_g$, where ψ is the angle between the osculating plane $(\mathbf{t}, \mathbf{n})$ and $\mathbf{e_1}$. The order parameter becomes the angle θ of the helix with its normal plane, and we are interested in computing θ as a function of α.

We construct a variational shape with two circular arcs joined by two helices with angle θ. Let ϵ be a variational parameter so that the length of each helix is $\pi R_0 \epsilon$. The angle ψ is taken to be constant in the two circular arcs ($\psi = \pm\psi_0$) and it varies linearly with the arclength in the two helices so that

$$\dot{\psi} = -\frac{\pi R_0 \epsilon}{2\psi_0}; \quad \frac{\pi}{2} R_0 (1-\epsilon) \leq s \leq \frac{\pi}{2} R_0 (1+\epsilon). \tag{7}$$

The total energy is thus a function of the three variational parameters $E(\theta, \psi_0, \epsilon)$. Numerical minimization of E gives that there exists a metastable state as long as $\alpha \leq= \alpha_c(3\mathrm{d}) = 0.9$. In the weak coupling regime, $\alpha \ll 1$, one finds $\cos(\theta) \simeq (\alpha)^{1/3}$ and the shape looks like two half circles of radius $\simeq R_0$ separated by two small straight helices ($\theta \simeq \pi/2$). In this limit, the width of the kink (anti-kink) tends to zero. In the opposite limit, where α approaches $\alpha_c(3\mathrm{d})$, the two helices degenerate into two circular arcs with $\theta = 0$. Obviously, the aspect ratio of the o-ring is important in this regime, since the o-ring cannot be self-intersecting. It is interesting to note that this model gives $\theta \simeq 1$ for $\alpha = 2/3$ (rubber case) with $\psi_0 = 0.7$. Within 5%, these are the values which are measured on a circular o-ring of Figure 1.

To conclude this paper, we study the case where the bend is induced by a concentration field. If φ denotes the variation with respect to its average value, the free energy decomposes into three parts. First, there is a concentration dependent intrinsic curvature $c_0(\varphi) = (\mathrm{d}c_0/\mathrm{d}\varphi)\,\varphi$. Second, there is a penalty term for the deviation with respect to the mean value $1/2a \oint \mathrm{d}s \left[\varphi^2 + \xi^{-2} (\nabla\varphi)^2\right]$. A Lagrange multiplier should also be included for the constraint on the total number of particles $(-\mu \int \mathrm{d}s\, \varphi)$. Neglecting the gradient term, we can minimize first with respect to φ to obtain an effective o-ring model with renormalized coefficients. Solving this model, we go back to the concentration field

$$\varphi = \frac{\mu + A\dot{\phi}\cos\psi}{\left(\frac{\mathrm{d}c_0}{\mathrm{d}\varphi}\right)^2 + a} \tag{8}$$

so that the concentration follows the deviation of the curvature. For $\oint \mathrm{d}s\varphi = 0$, we compute μ and use Figure 4 to show that φ is maximum at the two poles $(s = 0, \pi R_0)$.

In conclusion we have shown that an intrinsic curvature introduces a new lengthscale and leads to non-trivial metastable states, the simplest one being discussed in this paper.

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References

1. L. Landau, E. Lifchitz, *Théorie de l'élasticité* (Mir, Moscou, 1967). For a discussion of the Euler instability in the polymer case, see G.S. Manning, Phys. Rev. A **34**, 668 (1986).
2. I. Tobias, W.K. Olson, Biopolymers **33**, 639 (1993).
3. J. Bednar, P. Furrer, A. Stasiak, J. Dubochet, E.H. Egelman, A.D. Bates, J. Mol. Biol. **235**, 825 (1994).
4. See B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J.D. Watson, *Molecular Biology of the Cell*, second edition (Garland publishing, New York, 1989), p. 494.
5. F. Toulmé, E. Le Cam, C. Teyssier, E. Delain, P. Sautière, J.C. Maurizot and F. Culard, J. Bio. Chem. **270**, 6286, (1995); W. Han, S.M. Lindsay, M. Dlakic, R.E. Harrington, Nature **386**, 563 (1997).
6. J.F. Marko, E.D. Siggia, Macromolecules **27**, 981 (1994); J.F. Marko, E.D. Siggia, Phys. Rev. E **52**, 2912 (1995).
7. M. Lebret, Biopolymers **18**, 1709, 1979.
8. C.J. Benham, Biopolymers **22**, 2477, 1983.
9. J.H. White, A.M. J. Math. **91**, 693 (1969). See also reference [8].
10. H.T. Davis, *Introduction to Nonlinear Differential Equations and Integral Equations* (Dover, 1962).