Supporting Information for: Threading a Ring or a Tube onto a Rod: An Entropically Rare Event

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CALCULATION OF THE PARTITION FUNCTION FOR A RING ON A ROD

Using cylindrical polar coordinates (r, α, z) (figure 1) with the centre of the ring as the origin, and z pointing along a normal to the ring, and spherical polar coordinates for the relative direction of the ring and rod normals, gives a phase space volume:

$$Z_{on} = 2\int_0^L dx \int_0^{R-P} rdr \int_0^{2\pi} d\alpha \int_0^{2\pi} d\phi \int_0^{\theta_0} d\theta \sin\theta \tag{1}$$

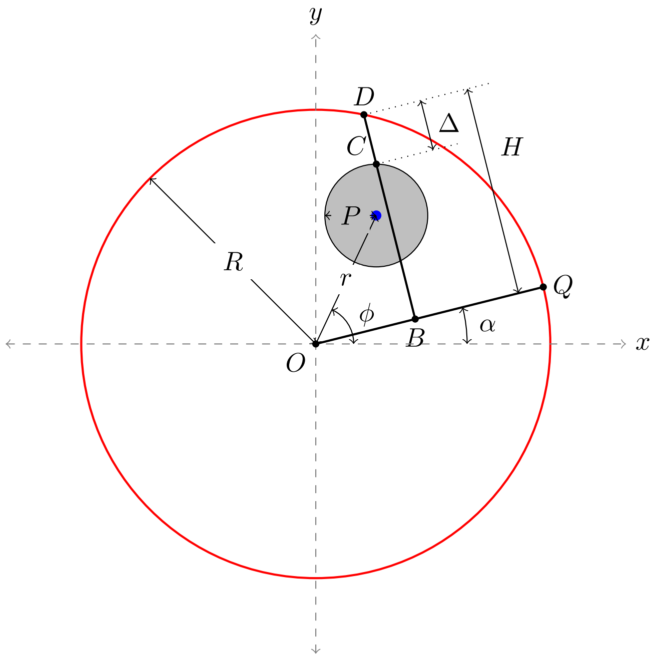

Figure 1: The geometry for the rod of radius P threading a ring (or tube) of radius R. The axis of the rod and the axis of the ring are aligned in the same direction, out of the page. We slowly rotate the axis of the ring about the line OQ. The rod will eventually come in to contact with the ring, and the point on the rod where this will happen can be found by minimising the distance DC=Δ.

Note that the integrals over x, r and α are over the position of the centre of the rod, relative to the centre of the ring. The remaining integrals are the orientation of

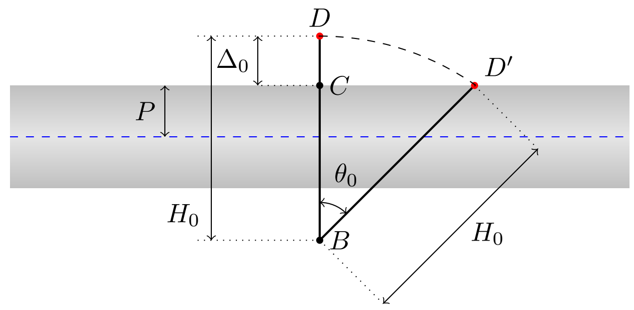

Figure 2: The geometry for the rod threading a ring, seen side on. The rod is in grey. DB is part of the ring seen in cross section, when the ring and rod are aligned. The ring then rotates about B until it touches the rod at D′. This defines the maximum rotation angle $\cos\theta_0 = (H_0 - \Delta_0)/H_0$.

the normal to the rod relative to that of the ring. The two can be aligned, $\theta = 0$, but they cannot point in any arbitrary direction, and so are limited to some value in the upper half plane, θ_0 (figure 2). In general θ_0 will depend on r, α and ϕ. The prefactor of two arises from the fact that the normal to the ring can either point in the upper half or lower half plane, and by symmetry each of these gives equal contribution. The integral over the rod length is just a constant factor L, the length of the rod. Also, it is clear that the value of θ_0 for a fixed r depends only on the difference $\phi - \alpha$ and not on ϕ and α separately (figure 1). It is thus possible to set $\alpha = 0$ (i.e. rotate about the x axis only) and replace the integral over α by a factor of 2π. Moreover by symmetry we only need to integrate over ϕ from 0 to $\pi/2$ and then multiply by 4. Finally we need

$$16\pi L \int_0^{R-P} rdr \int_0^{\pi/2} d\phi \int_{1-\Delta_0/H_0}^{1} d\cos\theta \tag{2}$$

We now need to calculate Δ_0 and H_0 (figure 1). With $\alpha = 0$ the point B varies along the x axis. Let $OB = x_B$. The equation of the rod surface is $(x - r\cos\phi)^2 + (y - r\sin\phi)^2 = P^2$ and so the point C has coordinates $(x_b, r\sin\phi + (P^2 - (x_B - r\cos\phi)^2)^{1/2})$. The point D has coordinates $(x_B, (R^2 - x_B^2)^{1/2})$. Thus $H = (R^2 - x_B^2)^{1/2}$ and $\Delta = (R^2 - x_B^2)^{1/2} - r\sin\phi - (\rho^2 - (x_B - r\cos\phi)^2)^{1/2}$. Minimising Δ over x_B gives $x_B = Rr\cos\phi/(R-P)$,

$\Delta_0 = (R^2 + P^2 - 2PR - r^2\cos^2\phi)^{1/2} - r\sin\phi$ and $H_0 = (R^2 - R^2 r^2\cos^2\phi/(R-P)^2)^{1/2}$. We thus need to perform the double integral $Z_{on} = 16\pi L R^2(1-\rho)I$ with

$$I = \int_0^{1-\rho} u du \int_0^{\pi/2} d\phi (1 - \frac{u\sin\phi}{\sqrt{(1-\eta)^2 - u^2\cos^2\phi}}) \quad (3)$$

which, defining $\rho \equiv P/R$, is $Z_{on} = 2R^2 L\pi^2(1-\rho)^3$. Thus the final answer for the 5-dimensional integral (1) is very simple.

CALCULATION OF THE PARTITION FUNCTION FOR A TUBE ON A ROD

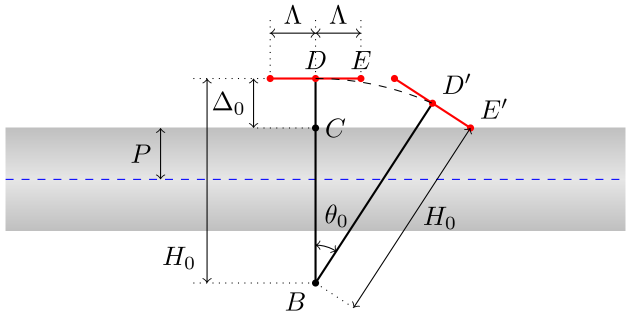

Figure 3: The geometry for the rod (in grey) threading a tube of length 2Λ), seen side on. The situation is almost identical to that for a ring, but now the rod collides with one end of the tube at E′

We slice the tube into two at the midpoint, so the cross section is just a ring of radius R (figure 1), and calculate Δ_0 and H_0, exactly as for the ring. However, when the tube is now tilted, it is one end of the tube which first contacts the rod (figure 3). From figure 3 θ_0 is given by $H_0 - \Delta_0 = H_0\cos\theta_0 - \Lambda\sin\theta_0$. Thus the integral over θ in (1) which is $1-\cos\theta_0$ yields:

$$(\Lambda^2 + H_0^2)^{-1}(H_0\Delta_0 + \Lambda^2 - \Lambda\sqrt{\Lambda^2 - \Delta_0^2 + 2H_0\Delta_0}) \quad (4)$$

We then need to integrate over r and ϕ, in (1) but once the r and ϕ dependence is explicit in the integrand it becomes lengthy (i.e. 95 lines of FORTRAN code). We thus resort to series expansions for small and large values of the parameters, and numerical calculation of the remaining integrals. The results are given in the main body of this work.

MONTE CARLO EVALUATION OF THE PARTITION FUNCTION

The problem is essentially two dimensional. A square box is chosen in the XY plane and a rod of radius P is placed at the origin, pointing normal to the plane. A ring of radius R is then chosen with a random centre, and normal pointing in a random direction (θ, ϕ) with θ and ϕ being the usual spherical polar angles, ϕ chosen uniformly between 0 and 2π, and $\cos\theta$ chosen uniformly between -1 and 1. We then test for threading as follows. If the centre of the ring is further than R from the origin, threading is not possible. Assuming this is not the case then we first check if the ring actually intersects the rod. In order to do this we step around the ring in small discrete steps, and see if any of these points (X_p, Y_p, Z_p) satisfy $X_p^2 + Y_p^2 < P^2$. If this is the case then the ring actually intersects the rod, and does not thread it. If it passes this test then we need to check for actual threading. To do this we take two random points on the ring, and draw a chord. If this chord intersects the rod, then the ring threads the rod. We repeat for many thousand random chords. If any of these intersect the rod then the ring threads the rod. The number of threaded rings is proportional to the desired partition function.

The process is the same for the tube, although here we need to check the ring at each end of the tube.

NUMERICAL EVALUATION OF THE PARTITION FUNCTION

We numerically evaluate the configurational volume of a ring threaded onto axle using two independent methods.

The first method counts the number of non-intersecting and threaded configurations by progressing orderly through a discretized configurational volume. We start with a ring of radius R in three dimensions, whose center is fixed at the origin and is initially oriented so that the normal to the ring is parallel to a threading axle. Let the axle be coincident with the z-axis, threading the interior of the ring at a coordinate (x_0, y_0). The complete configurational space of the axle-ring system is specified by the possible axle coordinates (x_0, y_0) and all possible orientations of the ring normal relative to the fixed axle, given by polar and azimuthal angles, (θ, ϕ). At each discretization of (x_0, y_0, θ, ϕ) we determine if the ring and axle are threaded without intersection. As the projection of the oriented ring onto a plane orthogonal to the axle is an ellipse, the aim is to determine if the cross section of the axle, a circle of radius a centered at $(x_0, y_0) \equiv \mathbf{x}_0$, is entirely within the interior the ellipse described by the parametric equation

$$\mathbf{x}(\Psi) = R[\mathbf{a}\cos\Psi + \mathbf{b}\sin\Psi].$$

where $\mathbf{a} \equiv (\cos\phi, \sin\phi)$ and $\mathbf{b} \equiv (-\cos\theta\sin\phi, \cos\theta\cos\phi)$ are the major and minor axes of the ellipse. That is, we've reduced the 3-dimensional problem of a ring and axle, to a 2-dimensional problem of a circle and an ellipse. To determine if the center of

the circle, $\mathbf{x}_0$, is inside the ellipse, we find the length of the line that runs from the ellipse center to the ellipse for which the $\mathbf{x}_0$ is co-linear. That length, p, is determined by

$$p = \frac{\mid \mathbf{a} \mid\mid \mathbf{b} \mid}{\sqrt{(\mid \mathbf{a} \mid \cos\gamma)^2 + (\mid \mathbf{b} \mid \sin\gamma)^2}}$$

where

$$\mathbf{x}_0 \cdot \mathbf{a} \equiv \mid \mathbf{x}_0 \mid\mid \mathbf{a} \mid \cos\gamma.$$

If $\mid \mathbf{x_0} \mid > p$, then the circle is outside of the ellipse and the axle outside of the ring. Once we've determined that the circle center is inside the ellipse, we need to determine if the circle intersects the ellipse. To do this we find the point on the ellipse which is closest to $\mathbf{x}_0$, that is we find $\Psi\prime$ for which $\mid \mathbf{x}_0 - \mathbf{x}(\Psi) \mid$ is minimal using a Newton minimisation. If that minimal distance is less than the circle radius, then the circle intersects the ellipse, and the axle intersects the ring.

To extend this calculation to a tube threaded by an axle, we describe a tube of radius R and length 2λ by a series of 3 rings, two at each end, and one at the middle. Again, we start with the tube or rings of radius R with center fixed at the origin and initially oriented so that the tube is parallel to the threading axle. Again, the axle is coincident with the z-axis, threading the interior of the rings at coordinates $(x_0, y_0, z_0 = \pm\lambda, 0)$. The complete configurational space of the axle-tube system is specified by the possible axle coordinates (x_0, y_0) and all possible orientations of the tube relative to the fixed axle, or equivalently all possible orientations of the normal of the middle ring (whose center is fixed at the origin) relative to the fixed axle, (θ, ϕ). At each descritization of (x_0, y_0, θ, ϕ) we determine if the cylinder and axle are threaded without intersection. To determine this, we again project the top and bottom faces of the cylinder (or rings) onto a plane orthogonal to the axle and check if the cross section of the axle, a circle of radius a centered at $(x_0, y_0) \equiv \mathbf{x}_0$, is entirely within the interior of two ellipses described by the parametric equation

$$\mathbf{x}(\Psi) = \mathbf{c} + R[\mathbf{a}\cos\Psi + \mathbf{b}\sin\Psi],$$

where the center of the top and bottom faces of the tubes are $\mathbf{c} \equiv \pm\lambda(\sin\theta\sin\phi, \sin\theta\cos\phi)$.

Short synopsis: We numerically evaluate the configurational volume of a ring threaded onto axle using two independent methods. The first method counts the number of non-intersecting and threaded configurations by progressing orderly through a discretized configurational space of four dimensions consisting of two coordinates that specify translation of the axle relative to the ring center and two more dimensions specifying the relative orientation of ring and axle. We determine those configurations that are threaded and non-intersecting by projecting the ring and axle from three to two dimensions, to give an ellipse and a circle, and checking that the axle radius is smaller than the minimum distance between circle center and any point on the ellipse using Newton minimisation. The configurational volume associated with a cyliinder threading an axle is similarly constructed as both faces of the cylinders serve as rings through which the axle must be threaded.