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**LETTER TO THE EDITOR**

# Free energy of a semiflexible polymer in a tube and statistics of a randomly-accelerated particle

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**Abstract.** The confinement free energy per unit length of a continuous semiflexible polymer or wormlike chain in a tube with a rectangular cross section is derived in the regime $P \gg L_1, L_2$ of strong confinement. Here $P$ is the persistence length, and $L_1$ and $L_2$ are the sides of the rectangle. The result is also interpreted in terms of the escape probability of a randomly-accelerated particle from a rectangular domain.

The statistical properties of a continuous semiflexible polymer or wormlike chain in a cylindrical tube have been studied with several equivalent theoretical approaches [1–5], reviewed in [6]. For a tube with a circular cross section of diameter $D$, the confinement free energy per unit length $\Delta f$ is given by

$$\Delta f = A_{\bigcirc} \frac{k_{\mathrm{B}}T}{P^{1/3}D^{2/3}} \qquad A_{\bigcirc} = 2.46 \pm 0.07 \tag{1}$$

in the regime $P \gg D$ of strong confinement, where the density of polymer-wall collisions is high. Here $P = \kappa/k_{\mathrm{B}}T$ is the persistence length, and $\kappa$ is the bending modulus. From dimensional analysis $\Delta f = k_{\mathrm{B}}T/\lambda$, where $\lambda$ is a length. As emphasized by Odijk [3, 6], the relevant physical length for a strongly confined polymer is not the persistence length $P$ but the typical distance $\lambda \sim P^{1/3}D^{2/3}$ between points where the polymer touches the tube.

For validity of the continuum description the tube diameter $D$ must be large in comparison with typical microscopic distances $a$, such as the monomer separation. Equation (1) is expected to hold for any semiflexible linear polymer in the regime $P \gg D \gg a$. The dimensionless constant $A_{\bigcirc}$ is a universal number, independent of both macroscopic and microscopic properties of the polymer chain. Its value is only known approximately. The estimate in equation (1) was obtained by Dijkstra *et al* [7] from computer simulations.

In this letter a semiflexible polymer in a tube with a rectangular cross section with edges $L_1$ and $L_2$ is considered. The rectangle leads to more tractable mathematics than the circle, and it is shown that $\Delta f$, including the universal amplitude $A_{\square}$, is exactly determined by a one-dimensional integral equation. A numerical solution of the integral equation yields

$$\Delta f = A_{\square} \frac{k_{\mathrm{B}}T}{P^{1/3}}(L_1^{-2/3} + L_2^{-2/3}) \qquad A_{\square} = 1.1036. \tag{2}$$

This is the main result of this letter. As discussed below, the result may also be interpreted in terms of the escape probability of an undamped Newtonian particle, moving in two dimensions and driven by Gaussian white noise, from a rectangular domain.

 

In specifying polymer configurations, it is convenient to use the three Cartesian coordinates $(\boldsymbol{x}, t) = (x_1, x_2, t)$, with the $t$-axis directed parallel to the tube. In the regime of strong confinement, configurations with overhangs are negligible, i.e. $\boldsymbol{x}$ is a single-valued function of $t$, and the partition function is given by the path integral [8]

$$Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t) = \int \mathrm{D}^2 x \exp\left\{ - \int_0^t \mathrm{d}t \left[ \frac{1}{2} P \left( \frac{\mathrm{d}^2 \boldsymbol{x}}{\mathrm{d}t^2} \right)^2 + V(\boldsymbol{x}) \right] \right\}. \tag{3}$$

Here $\boldsymbol{x}$ and $\boldsymbol{u} = \mathrm{d}\boldsymbol{x}/\mathrm{d}t$ denote the displacement and slope of the polymer at $t$, and $\boldsymbol{x}_0$ and $\boldsymbol{u}_0$ the same quantities at $t = 0$. The two terms in the exponential function represent the bending energy and the potential energy leading to confinement, both divided by $k_\mathrm{B}T$. The path integral implies the partial differential equation [8–12]

$$\left[ \frac{\partial}{\partial t} + \boldsymbol{u} \cdot \nabla_{\boldsymbol{x}} - \frac{1}{2P} \nabla_{\boldsymbol{u}}^2 + V(\boldsymbol{x}) \right] Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t) = 0 \tag{4}$$

with the initial condition

$$Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; 0) = \delta(\boldsymbol{x} - \boldsymbol{x}_0)\delta(\boldsymbol{u} - \boldsymbol{u}_0). \tag{5}$$

Equation (4) is readily solved in the cases $V(\boldsymbol{x}) = 0$ and $V(\boldsymbol{x}) = \frac{1}{2} b \boldsymbol{x}^2$ of a free [8] and a harmonically confined polymer [13], respectively. The exact solution [14] for a polymer confined to the half space $x_2 > 0$ is considerably more complex, due to the hard-wall boundary condition. Polymer configurations with a discontinuity in slope cost an infinite energy according to equation (3) and are completely suppressed. This implies [14] that $Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t)$ vanishes for $\boldsymbol{u} \cdot \boldsymbol{n} > 0$ as $\boldsymbol{x}$ approaches a hard wall. This requirement and the differential equation (4) with (5) determine the non-zero but initially unspecified value of $Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t)$ on the boundary for $\boldsymbol{u} \cdot \boldsymbol{n} < 0$. Here $\boldsymbol{n}$ is a unit vector perpendicular to the boundary surface and directed into the region accessible to the polymer. In this letter a polymer in a tube with a rectangular cross section, i.e. four hard walls, is considered. The confining potential is given by

$$V(\boldsymbol{x}) = \begin{cases} 0 & 0 < x_1 < L_1, 0 < x_2 < L_2 \\ \infty & \text{otherwise.} \end{cases} \tag{6}$$

In analysing long polymer chains it is convenient to look for exponentially decaying solutions of equation (4) with the form $\Psi(\boldsymbol{x}, \boldsymbol{u}) \exp(-Et)$. The eigenfunctions $\Psi_n$ and eigenvalues $E_n$ satisfy

$$\left[ \boldsymbol{u} \cdot \nabla_{\boldsymbol{x}} - \frac{1}{2P} \nabla_{\boldsymbol{u}}^2 + V(\boldsymbol{x}) - E_n \right] \Psi_n(\boldsymbol{x}, \boldsymbol{u}) = 0. \tag{7}$$

In the long polymer limit the partition function and the confinement free energy per unit length are given by

$$Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t) \approx \text{constant} \times \Psi_0(\boldsymbol{x}, \boldsymbol{u}) \Psi_0(\boldsymbol{x}_0, -\boldsymbol{u}_0)\, \mathrm{e}^{-E_0 t} \qquad t \to \infty \tag{8}$$

$$\frac{\Delta f}{k_\mathrm{B}T} = - \lim_{t \to \infty} t^{-1} \ln Z(\boldsymbol{x}, \boldsymbol{u}; \boldsymbol{x}_0, \boldsymbol{u}_0; t) = E_0 \tag{9}$$

where $E_0$ is the eigenvalue with the smallest real part. The eigenvalues $E_n$ are, in general, complex. However, for a non-negative confining potential, $E_0$ is positive and non-degenerate, due to the real, non-negative argument of the exponential function in the path integral (3).

In its statistical properties the semiflexible polymer is equivalent to a randomly accelerated particle moving in two dimensions. Consider an undamped particle of unit mass moving according to the Newtonian equations of motion $\mathrm{d}^2 x_i/\mathrm{d}t^2 = \xi_i(t)$ in the unbounded two-dimensional space $(x_1, x_2)$. Let $\xi_i(t)$ be a Gaussian random force with zero mean and correlation function $\langle \xi_i(t)\xi_j(t')\rangle = P^{-1}\delta_{ij}\delta(t-t')$. The probability density in $(\boldsymbol{x}, \boldsymbol{u})$ space that the particle remains in the rectangular domain $0 < x_1 < L_1$, $0 < x_2 < L_2$ for a time $t$ while the position and velocity evolve from $(\boldsymbol{x}_0, \boldsymbol{u}_0)$ to $(\boldsymbol{x}, \boldsymbol{u})$ satisfies a Fokker–Planck equation with exactly the form (4) and (5) and the same boundary condition (see above) as the polymer partition function at the hard walls [15, 16]. For long times the probability that the particle has not yet left the rectangular domain decays as $\exp(-E_0 t)$, as follows from equation (8). Recently, Masoliver and Porrà [16] gave an exact derivation of the mean escape time of a particle moving in one dimension and driven by Gaussian white noise from the line segment $0 < x < L$. In this letter the decay constant $E_0$ is derived with a very similar approach.

For the rectangular confining potential (6), equation (7) has the separable solution

$$\Psi_0(\boldsymbol{x}, \boldsymbol{u}) = \psi(x_1, u_1; L_1)\psi(x_2, u_2; L_2) \qquad E_0 = \epsilon_0(L_1) + \epsilon_0(L_2) \tag{10}$$

where

$$\left[u_i \frac{\partial}{\partial x_i} - \frac{1}{2P}\frac{\partial^2}{\partial u_i^2} - \epsilon_0(L_i)\right]\psi(x_i, u_i; L_i) = 0 \qquad 0 < x_i < L_i \tag{11}$$

with $i = 1, 2$. On rescaling the rectangle into a square and introducing dimensionless variables $\ell$, $y_i = \ell(x_i/L_i)$, $v_i = (2\ell P/L_i)^{1/3}u_i$, equations (10) and (11) are replaced by

$$\Psi_0(\boldsymbol{x}, \boldsymbol{u}) = \psi(y_1, v_1)\psi(y_2, v_2) \qquad E_0 = \ell^{2/3}(2P)^{-1/3}(L_1^{-2/3} + L_2^{-2/3}) \tag{12}$$

$$\left(v\frac{\partial}{\partial y} - \frac{\partial^2}{\partial v^2} - 1\right)\psi(y, v) = 0 \qquad 0 < y < \ell. \tag{13}$$

The function $\psi(y, v)$ satisfies the hard-wall boundary conditions

$$\psi(0, v) = 0 \quad v > 0 \qquad \psi(\ell, v) = 0 \quad v < 0 \tag{14}$$

discussed just above equation (6). Note that the dependence of $\Delta f/k_\mathrm{B}T = E_0$ on the physical parameters $P$, $L_1$ and $L_2$ is already quite explicit in equation (12) and similar to (2). The eigenvalue $\epsilon(L_i)$ in equations (10) and (11) does not appear in (13). The problem of calculating the eigenvalue has been replaced by the problem of determining the dimensionless interval width $\ell$ for which (13) and (14) have a physical solution.

Following Masoliver and Porrà [16], we solve the differential equation (13) and (14) for $v > 0$ and extend the solution to negative $v$ using the symmetry property

$$\psi(y, v) = \psi(\ell - y, -v) \tag{15}$$

which follows from the invariance of the confining potential under $y \to \ell - y$. It is convenient to continue $\psi(y, v)$ for $v > 0$ from $0 < y < \ell$ to $y > \ell$ and consider the Laplace transform

$$\hat{\psi}(s, v) = \int_0^\infty \mathrm{d}y\, \mathrm{e}^{-sy}\psi(y, v) \tag{16}$$

which satisfies the Airy differential equation [17]

$$\left(sv - \frac{\partial^2}{\partial v^2} - 1\right)\hat{\psi}(s, v) = 0. \tag{17}$$

The physical solution, which vanishes for $v \to \infty$, is $\hat{\psi}(s, v) = W(s)\mathrm{Ai}(s^{1/3}v - s^{-2/3})$, where $\mathrm{Ai}(z)$ is the standard Airy function [17] and $W(s)$ is a weight function to be determined. With equal generality one may write

$$\hat{\psi}(s, v) = s^{-1/3}\frac{\mathrm{Ai}(s^{1/3}v - s^{-2/3})}{\mathrm{Ai}'(-s^{-2/3})}\frac{\partial\hat{\psi}(s, 0)}{\partial v}. \tag{18}$$

According to the Faltung theorem [17] the inverse Laplace transform of equation (18) has the form

$$\psi(y, v) = -\int_0^y \mathrm{d}y' K(y - y', v) \frac{\partial \psi(y', 0)}{\partial v} \tag{19}$$

$$K(y, v) = -\int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \frac{\mathrm{d}s}{2\pi \mathrm{i}} s^{-1/3} \frac{\mathrm{Ai}(s^{1/3}v - s^{-2/3})}{\mathrm{Ai}'(-s^{-2/3})} \mathrm{e}^{ys}. \tag{20}$$

Compensating minus signs have been introduced in equations (19) and (20) so that the quantity $K(y, 0)$ defined by (20) is positive. Note that $\psi(y, v)$ as given by equation (19) for $v > 0$ satisfies the hard-wall boundary condition (14) at $y = 0$.

An integral equation for the unknown function $\partial\psi(y', 0)/\partial v$ in equation (19), may be derived as follows. From (15), $\psi(y, 0) - \psi(\ell - y, 0) = 0$. Expressing the two terms on the left-hand side of this relation as integrals of $\partial\psi(y', 0)/\partial v$ using (19) and substituting $\partial\psi(y', 0)/\partial v = -\partial\psi(\ell - y', 0)/\partial v$, which also follows from (15), leads to

$$\int_0^{\ell/2} \mathrm{d}y' \left[K(|y - y'|, 0) - K(|\ell - y - y'|, 0)\right] \frac{\partial \psi(y', 0)}{\partial v} = 0. \tag{21}$$

To solve the integral equation (21), one must first calculate $K(y, v)$, defined by (20). This was done numerically, after deforming the integration contour to pass just below and above the real $s$-axis, enclosing the poles and branch cut [17] of the integrand. The numerical procedure was checked by direct numerical integration of (20) in the complex $s$ plane using *Mathematica*. For $y \geqslant 0$ and $v \geqslant 0$, $K(y, v)$ is well behaved except at $y = 0$. The asymptotic form of the integrand in (20) for large $s$ contributes the leading singular term

$$K(y, v)_{\mathrm{sing}} = ky^{-2/3} \exp(-v^3/9y) \qquad k = -\Gamma(\tfrac{1}{3})^{-1}\mathrm{Ai}(0)\mathrm{Ai}'(0)^{-1} = 0.512\,039\,06 \tag{22}$$

at $y = 0$. The function $K(y, 0)$ is shown in figure 1, with and without subtraction of the singular contribution (22).

Equations (15) and (21) and the singular term $ky^{-2/3}$ in $K(y, 0)$ imply the leading singular behaviour $\partial\psi(y, 0)/\partial y \sim [y(\ell - y)]^{-1/6}$ at $y = 0, \ell$, encountered previously in [8, 12, 14, 16]. It is convenient to consider the function $g(y) = -g(\ell - y)$ defined by

$$\frac{\partial \psi(y, 0)}{\partial y} = [y(\ell - y)]^{-1/6} g(y). \tag{23}$$

Both $g(y)$ and its derivative $g'(y)$ turn out to be smooth and finite at $y = 0, \ell$.

The integral equation (21) with substitution (23) was solved numerically by approximating it with a difference equation of the form

$$\sum_j w(y_i, y_j) g(y_j) = 0 \qquad y_i = i\ell/(2N) \qquad i, j = 0, 1, 2, \ldots, N. \tag{24}$$

Taking the singularities (22) and (23) into account, the weights $w(y_i, y_j)$ were chosen according to a four-point quadrature rule (see [18], equation (18.3.5)), so that the sum in (24) exactly reproduces the integral in (21) for all functions $g(y)$ that have the form of piecewise-continuous third-order polynomials. Since the exact $g(y)$ is a smooth function, good numerical precision is achieved, even for small $N$.

For small $\ell$ and fixed $N$ all eigenvalues of the matrix $w(y_i, y_j)$ are positive, and the only solution of the difference equation (24) is the trivial solution $g(y_i) = 0$. As $\ell$ increases, the smallest eigenvalue becomes negative. The critical value of $\ell$ at which the eigenvalue vanishes converges rapidly with increasing $N$ to 1.6396. Inserting this value in equation (12) and making use of (9), one obtains $A_\Box = 1.1036$ for the universal amplitude in (2).

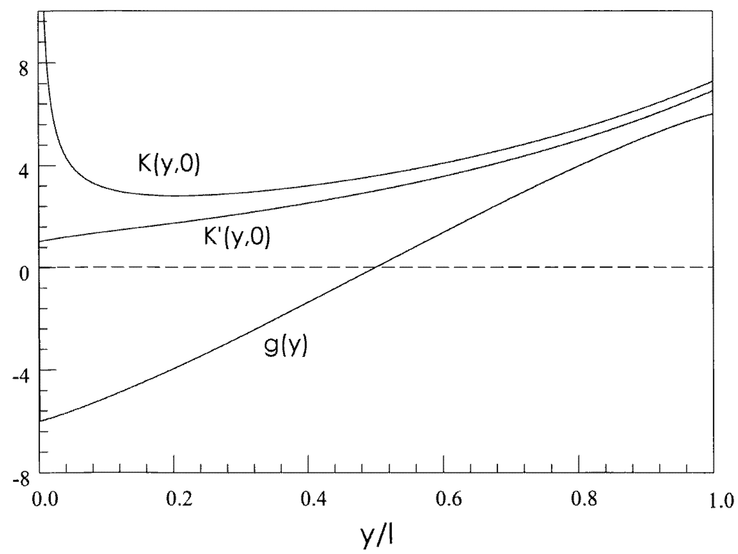


**Figure 1.** The functions $K(y,0)$, $K'(y,0) = K(y,0) - K_{\mathrm{sing}}(y,0)$, and $g(y)$, defined by equations (20)–(23), for $0 < y/\ell < 1$.

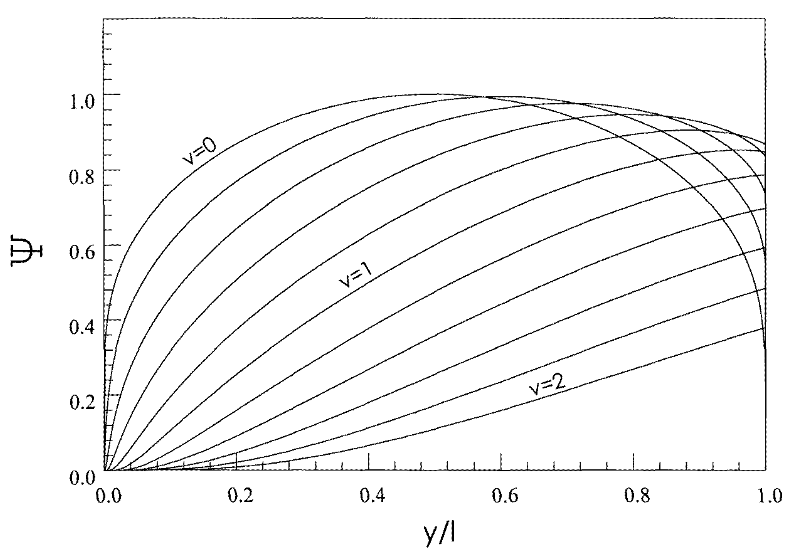


**Figure 2.** The function $\psi(y,v)$, defined by equations (12)–(14), for $0 < y/\ell < 1$ and $v = 0.0$, 0.2, 0.4, …, 2.0, normalized so that $\psi(\ell/2, 0) = 1$.

At the critical value of $\ell$ the integral equation (21), (23) has the non-trivial solution $g(y)$ shown in figure 1. The solution is an odd function of $y - \ell/2$, as expected from (15) and (23), and is smooth and roughly linear.

The eigenfunction $\psi(y,v) = \psi(\ell - y, -v)$, which through (8) and (12) directly determines the partition function of a long confined polymer, is shown as a function of $y/\ell$ for $v = 0.0, 0.2, \ldots, 2.0$ in figure 2. In accordance with the hard-wall boundary condition (14), $\psi(\ell, v)$ vanishes for negative $v$. For positive $v$, $\psi(\ell, v)$ has a maximum for a value of $v$ between 0.6 and 0.8. This reflects the tendency of a long polymer to slope outward from the interior of the tube towards a fixed endpoint on the wall of the tube.

Finally, we compare the result $A_{\bigcirc} = 2.46 \pm 0.07$ of Dijkstra *et al* [7] from computer simulations and our result $A_{\Box} = 1.1036$ with some rigorous inequalities. Both predictions are consistent with the lower bounds

$$A_{\bigcirc} > \frac{3}{2} \qquad A_{\Box} > \frac{3}{2^{7/3}} = 0.595\,28 \tag{25}$$

which follow [13] from the exact confinement free energy of a semiflexible polymer in a harmonic potential. The inequalities

$$2A_{\Box} < A_{\bigcirc} < 2^{4/3} A_{\Box} \tag{26}$$

reflect the fact that a tube with a circular cross section of diameter $D$ is more confining than a tube with a square cross section and edge $D$ and less confining than a tube with a square cross section and edge $D/\sqrt{2}$, i.e. $Z_{\Box}(D) > Z_{\bigcirc}(D) > Z_{\Box}(D/\sqrt{2})$. Inserting our result for $A_{\Box}$, thought to be exact to five significant figures, in equation (26) yields $2.2072 < A_{\bigcirc} < 2.7809$. The estimate $A_{\bigcirc} = 2.46 \pm 0.07$ is clearly consistent with these bounds.

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