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Simulation of a semiflexible polymer in a narrow cylindrical pore

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Received 11 April 2001

Published 13 July 2001

Online at stacks.iop.org/JPhysA/34/5745

Abstract

The probability that a randomly accelerated particle in two dimensions has not yet left a simply connected domain \mathcal{A} after a time t decays as $e^{-E_0 t}$ for long times. The same quantity E_0 also determines the confinement free energy per unit length $\Delta f = k_B T E_0$ of a semiflexible polymer in a narrow cylindrical pore with cross section \mathcal{A} . From simulations of a randomly accelerated particle we estimate the universal amplitude of Δf for both circular and rectangular cross sections.

PACS numbers: 36.20.Ey, 05.10.-a, 05.10.Gg, 05.70.Ce

(Some figures in this article are in colour only in the electronic version)

Consider a long semiflexible polymer with persistence length P fluctuating in a cylindrical pore with diameter D . In the narrow-pore limit $D \ll P$ the free energy of confinement per unit length Δf is given by

$$\Delta f = A_{\circ} \frac{k_B T}{P^{1/3} D^{2/3}}. \quad (1)$$

This follows from simple scaling or dimensional arguments [1–3], such as that given below. Similarly, for a pore with a rectangular cross section [3] with edges $L_1, L_2 \ll P$

$$\Delta f = A_{\square} \frac{k_B T}{P^{1/3}} \left(\frac{1}{L_1^{2/3}} + \frac{1}{L_2^{2/3}} \right). \quad (2)$$

The dimensionless constants A_{\circ} , A_{\square} in equations (1) and (2) are universal numbers, independent of both macroscopic and microscopic properties of the polymer chain. From computer simulations Dijkstra *et al* [2] estimated

$$A_{\circ} = 2.46 \pm 0.07. \quad (3)$$

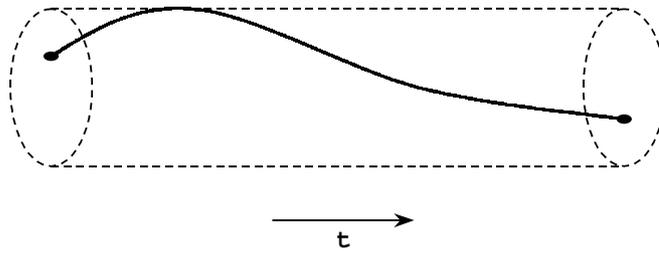


Figure 1. The curve may be interpreted as a tightly confined semiflexible polymer in a cylindrical pore with cross section \mathcal{A} or as the world line of a particle which is randomly accelerated in two dimensions and remains in a domain \mathcal{A} for a time t .

Solving an integral equation numerically that arises in an exact analytical approach, Burkhardt [3] obtained

$$A_{\square} = 1.1036. \quad (4)$$

In the Monte Carlo simulations of Dijkstra *et al* [2], polymer configurations consistent with the Boltzmann distribution were generated with a Metropolis algorithm incorporating detailed balance. In this letter we estimate A_{\circ} , A_{\square} with a precision of about 1% using a Langevin dynamics approach, which is simple and efficient. Instead of a confined semiflexible polymer, we simulate a Newtonian particle which is randomly accelerated by Gaussian white noise in two dimensions. In the narrow-pore or tight-confinement limit these two systems have equivalent statistical properties, as discussed in [3] and reviewed below. The basic idea, illustrated in figure 1, is that each of the possible world lines of a particle, which is randomly accelerated in two dimensions and remains in a domain \mathcal{A} for a time t , corresponds to an allowed configuration of a tightly confined semiflexible polymer in a cylindrical pore or tube with cross section \mathcal{A} .

We now describe the correspondence in more detail. As in [3], polymer configurations are specified in terms of Cartesian coordinates $(\mathbf{x}, t) = (x_1, x_2, t)$. The t axis is parallel to the axis of the cylindrical pore, as shown in figure 1. In the narrow-pore limit $D \ll P$ or $L_1, L_2 \ll P$, configurations with overhangs are negligible, i.e. \mathbf{x} is a single-valued function of t . The partition function is given by the path integral [3]

$$Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t) = \int_{\mathcal{A}} D^2x \exp \left[-\frac{1}{2} P \int_0^t dt \left(\frac{d^2\mathbf{x}}{dt^2} \right)^2 \right] \quad (5)$$

where \mathbf{x} and $\mathbf{u} = d\mathbf{x}/dt$ denote the displacement and slope of the polymer at t , and \mathbf{x}_0 and \mathbf{u}_0 the same quantities at $t = 0$. A hard-wall-confining potential is assumed, and the \mathbf{x} integration is limited to the domain \mathcal{A} .

The path integral implies the partial differential equation [3–8]

$$\left[\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla_{\mathbf{x}} - \frac{1}{2P} \nabla_{\mathbf{u}}^2 \right] Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t) = 0 \quad (6)$$

to be solved with the initial condition

$$Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; 0) = \delta(\mathbf{x} - \mathbf{x}_0) \delta(\mathbf{u} - \mathbf{u}_0). \quad (7)$$

Since the polymer is confined to the interior of the pore and configurations with a discontinuity in slope cost an infinite energy, $Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t)$ vanishes for $\mathbf{u} \cdot \mathbf{n} > 0$ as \mathbf{x} approaches a hard wall. Here \mathbf{n} is a vector normal to the wall and directed toward the interior of the pore.

As in [3] we consider exponentially decaying solutions of equation (6) with the form $\psi(\mathbf{x}, \mathbf{u}) \exp(-Et)$. The eigenfunctions ψ and eigenvalues E_n satisfy

$$\left[\mathbf{u} \cdot \nabla_{\mathbf{x}} - \frac{1}{2P} \nabla_{\mathbf{u}}^2 - E_n \right] \psi_n(\mathbf{x}, \mathbf{u}) = 0 \quad (8)$$

where $\psi(\mathbf{x}, \mathbf{u})$ also vanishes for $\mathbf{u} \cdot \mathbf{n} > 0$ as \mathbf{x} approaches the pore wall. In the long-polymer limit the partition function and the confinement free energy per unit length are given by

$$Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t) \approx \text{const} \times \psi_0(\mathbf{x}, \mathbf{u}) \psi_0(\mathbf{x}_0, -\mathbf{u}_0) e^{-E_0 t} \quad t \rightarrow \infty \quad (9)$$

$$\frac{\Delta f}{k_B T} = E_0(P, D) \quad (10)$$

for a pore with a circular cross section of diameter D , where E_0 is the smallest of the eigenvalues E_n .

The P and D dependence in equation (1) may be derived from (10) by making the scale change $\mathbf{x} = \alpha \mathbf{x}'$, $\mathbf{u} = \beta \mathbf{u}'$ in (8), where α and β are arbitrary positive constants. This leads to the scaling property

$$E_n(P, D) = \alpha^{-1} \beta E_n(\alpha^{-1} \beta^3 P, \alpha^{-1} D) \quad (11)$$

of the eigenvalues. Setting $\alpha = D$ and $\beta = P^{-1/3} D^{1/3}$ in equation (11) and substituting the result in (10), we obtain

$$\frac{\Delta f}{k_B T} = \frac{E_0(1, 1)}{P^{1/3} D^{2/3}}. \quad (12)$$

This expression is entirely consistent with equation (1) and implies

$$A_{\circ} = E_0(1, 1). \quad (13)$$

Similarly, for a pore with a rectangular cross section

$$2A_{\square} = E_0(1, 1, 1) \quad (14)$$

where $E_0(P, L_1, L_2)$ denotes the smallest eigenvalue in equation (8) for a rectangular domain with edges L_1, L_2 . Equations (13) and (14) allow us to determine the universal amplitudes A_{\circ} and A_{\square} from calculations with $P = D = L_1 = L_2 = 1$.

For the rectangular domain equation (8) has separable eigenfunctions $\psi_{m,n}(\mathbf{x}, \mathbf{u}) = \phi_m(x_1, u_1) \phi_n(x_2, u_2)$, with eigenvalues $E_{m,n} = E_m^{(1 \text{ dim})}(P, L_1) + E_n^{(1 \text{ dim})}(P, L_2)$, where

$$\left[u \frac{\partial}{\partial x} - \frac{1}{2P} \frac{\partial^2}{\partial u^2} - E_m^{(1 \text{ dim})}(P, L) \right] \phi_m(x, u) = 0. \quad (15)$$

Here $0 < x < L$, and $\phi(x, u)$ vanishes for $x = 0, u > 0$ and $x = L, u < 0$. Thus equation (14) may be rewritten as

$$A_{\square} = E_0^{(1 \text{ dim})}(1, 1) \quad (16)$$

in terms of the smallest eigenvalue of (15) for $P = L = 1$. The earlier numerical result for A_{\square} , noted in equation (4), was obtained in [3] by converting (15) to an integral equation, determining the smallest eigenvalue numerically, and substituting the result in (16).

Now consider a particle which is randomly accelerated in the d -dimensional space (x_1, \dots, x_d) by Gaussian white noise with zero mean according to

$$\frac{d^2 x_i}{dt^2} = \xi_i(t) \quad \langle \xi_i(t) \xi_j(t') \rangle = P^{-1} \delta_{ij} \delta(t - t'). \quad (17)$$

The probability density in phase space (\mathbf{x}, \mathbf{u}) that the particle remains in the domain \mathcal{A} for a time t while the position and velocity evolve from $(\mathbf{x}_0, \mathbf{u}_0)$ to (\mathbf{x}, \mathbf{u}) satisfies a Fokker–Planck

equation [8] with exactly the same form (6), initial condition (7), and boundary condition at the boundary of \mathcal{A} . Thus the probability density of the randomly accelerated particle equals the partition function of a semiflexible polymer in a pore with cross section \mathcal{A} and decays as $\exp(-E_0 t)$ for long times, as in equation (9).

To estimate A_{\square} using equation (16), we simulated a randomly accelerated particle in one spatial dimension. From simulations in two dimensions we obtained a second estimate of A_{\square} based on (14) and a prediction for A_{\circ} from (13). The simulation routine, similar to that in [9], will now be described briefly.

In an unbounded d -dimensional space the exact solution of the Fokker–Planck equation (6) with initial condition (7) and with $P = 1$ is given by [4, 10]

$$Z_{\text{free}}(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t) = \left(\frac{3^{1/2}}{\pi t^2} \right)^d \times \exp \left\{ -\frac{6}{t^3} \left[(\mathbf{x} - \mathbf{x}_0 - \mathbf{u}_0 t) \cdot (\mathbf{x} - \mathbf{x}_0 - \mathbf{u} t) + \frac{1}{3} (\mathbf{u} - \mathbf{u}_0)^2 t^2 \right] \right\}. \quad (18)$$

Trajectories with the probability distribution $Z_{\text{free}}(\mathbf{x}_{n+1}, \mathbf{u}_{n+1}; \mathbf{x}_n, \mathbf{u}_n; \Delta_{n+1})$ given by (18) are generated using the algorithm

$$\mathbf{x}_{n+1} = \mathbf{x}_n + \mathbf{u}_n \Delta_{n+1} + \mathbf{e}_n \Delta_{n+1}^{3/2} (3^{-1/2} s_{n+1} + r_{n+1}) \quad (19)$$

$$\mathbf{u}_{n+1} = \mathbf{u}_n + \mathbf{e}_n 2 \Delta_{n+1}^{1/2} r_{n+1} \quad (20)$$

where \mathbf{x}_n and \mathbf{u}_n are the position and velocity of the particle at time t_n , and $\Delta_{n+1} = t_{n+1} - t_n$. The quantity \mathbf{e}_n is a unit vector that points either along the positive x_1 axis, the positive x_2 axis, . . . , or the positive x_d axis with equal probability, and r_n and s_n are independent Gaussian random numbers satisfying

$$\langle r_n \rangle = \langle s_n \rangle = 0 \quad \langle r_n^2 \rangle = \langle s_n^2 \rangle = 1. \quad (21)$$

In the absence of boundaries there is no time-step error in the above algorithm, i.e. the Δ_n may be chosen arbitrarily. Close to the boundaries small time steps are needed. As in [9] we performed our simulations with

$$\Delta_{n+1} = 10^{-5} + 10^{-1} D_n \quad (22)$$

where D_n is the distance from the particle to the closest point of the domain boundary at time t_n . This time step fulfils a reliability criterion discussed in [9].

Some sample simulation results are shown in figure 2. The quantity $Q(t)$ is the probability that a particle with a random initial position in a one- or two-dimensional domain and with initial velocity zero, which is randomly accelerated according to equation (17) with $P = 1$, has not yet left the domain after a time t . The curves labelled ‘circle’, ‘square’ and ‘interval’ refer to a circular domain of diameter $D = 1$, a square with edges $L_1 = L_2 = 1$, and a one-dimensional interval of length $L = 1$. Each of the curves is based on 10 000 independent trajectories.

Since $Q(t) = \int d^d x \int d^d u \int d^d x_0 Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{0}; t)$, it decays as $e^{-E_0 t}$ for long times, with the same decay constant E_0 as $Z(\mathbf{x}, \mathbf{u}; \mathbf{x}_0, \mathbf{u}_0; t)$ in equation (9). We determined E_0 for the circular, square and one-dimensional domains by fitting $Q(t)$ for long times with an exponential function. A surprising result, shown in figure 2, is that the curves for the circular and square domains practically coincide when plotted versus $E_0 t$ instead of t .

We also estimated E_0 for circular, square and one-dimensional domains from trajectories that all begin at the the centre of the domain with initial velocity zero. The results are consistent with the results for random initial positions but have a somewhat greater statistical uncertainty.

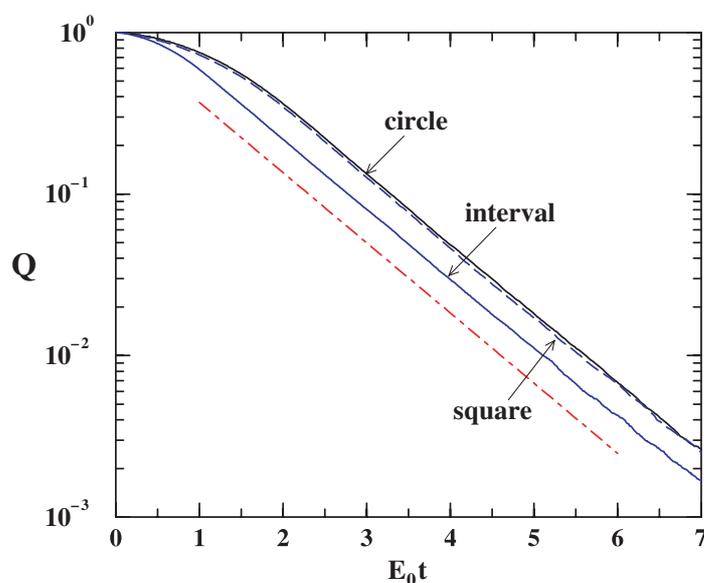


Figure 2. Probability $Q(t)$ that a particle with random initial position in a one- or two-dimensional domain and initial velocity zero, which is randomly accelerated according to equation (17) with $P = 1$, has not yet left the domain after a time t . The curves labelled ‘circle’ (full curve), ‘square’ (broken curve), and ‘interval’ (full curve) correspond to a circular domain with diameter 1, a square domain with edge 1, and a one-dimensional interval with length 1. For the three curves $E_0 = 2.375, 2.199, 1.108$, respectively. The chain curve represents a pure exponential decay $e^{-E_0 t}$.

Combining our best estimates of E_0 with equations (13), (14) and (16), we obtain

$$A_{\circ} = 2.375 \pm 0.013 \quad (23)$$

$$A_{\square} = 1.108 \pm 0.013. \quad (24)$$

The result (23) for A_{\circ} is somewhat lower than the estimate (3) of Dijkstra *et al* [2] and has a smaller statistical uncertainty. The result (24) for A_{\square} in the equation is consistent with the value (4) obtained by Burkhardt from the numerical solution of an exact integral equation [3]. Bundschuh [11] has also confirmed (4) to within a few percent with a numerical transfer matrix approach [12] for semiflexible polymers.

In summary, we have found a simple and efficient simulational procedure for calculating the confinement free energy of a semiflexible polymer in a narrow cylindrical pore with cross section \mathcal{A} . We use the equivalent statistical properties of a Newtonian particle which is randomly accelerated by Gaussian white noise in two dimensions. The probability that the particle has not yet left a domain \mathcal{A} in a time t decays as $e^{-E_0 t}$. We determine E_0 from our simulations and then interpret it, following equation (10), in terms of the polymer free energy. We emphasize that the equivalence between the statistics of the polymer and the randomly accelerated particle is asymptotically exact in the limit in which the pore diameter is much smaller than the polymer persistence length.

Acknowledgments

TWB appreciates the hospitality of the Institut Laue-Langevin, where this work was begun, and thanks Ralf Bundschuh for helpful correspondence.

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