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LETTER TO THE EDITOR

Semiflexible polymer in the half plane and statistics of the integral of a Brownian curve

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Abstract. A continuum model of a polymer with non-zero bending energy, fluctuating without overhangs in the half plane, is considered. The exact partition function is obtained from the Marshall–Watson solution of the Klein–Kramers equation for Brownian motion in the half space. The partition function contains information on probabilities associated with the integral of a Brownian curve and reproduces Sinai's $t^{-5/4}$ result for the asymptotic first passage time density. The $t^{-5/2}$ dependence of a different passage probability implies a first-order polymer adsorption transition for short-range pinning potentials.

In this letter a simple continuum model of a linear polymer with non-zero bending energy, fluctuating without overhangs in the half plane $x > 0, -\infty < t < \infty$, is considered. Here x and t are Cartesian length coordinates, and polymer configurations without overhangs correspond to single-valued functions $x(t)$. The partition function of the polymer is given by the path integral

$$Z(x,u;x_0,u_0;t) = \int \mathrm{D}x \exp\left\{-\int_0^t \mathrm{d}t \left[\frac{1}{2}\kappa\left(\frac{\mathrm{d}^2x}{\mathrm{d}t^2}\right)^2 + V(x)\right]\right\} \tag{1}$$

where x and $u = \mathrm{d}x/\mathrm{d}t$ denote the displacement and slope of the polymer at t, and x_0 and u_0 the same quantities at $t = 0$. The parameter κ specifies the bending energy, and $V(x)$ is a potential energy.

The adsorption transition in this model has been studied for various classes of pinning potentials by Maggs *et al* [1] and by Gompper and Burkhardt [2] with approaches that are partially numerical. In this letter a complete analytic solution for short-range potentials is given, and a connection with the statistics of the integral of a Brownian curve is pointed out.

In the case of 'directed polymers' [3–5] the action is the same as in equation (1) except that $(\mathrm{d}^2x/\mathrm{d}t^2)^2$ is replaced by $(\mathrm{d}x/\mathrm{d}t)^2$. The statistical weight $Z(x,x_0;t)$ for directed polymers satisfies Schrödinger's equation. Equation (1) leads to the more complicated partial differential equation [1,2]

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} - \frac{1}{2\kappa}\frac{\partial^2}{\partial u^2} + V(x)\right] Z(x,u;x_0,u_0;t) = 0. \tag{2}$$

The factor $(2\kappa)^{-1}$ can be eliminated from equation (2) by rescaling x, u, t and $V(x)$ and will be omitted from now on.

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Polymer configurations with discontinuities in slope cost an infinite energy according to equation (1) and are completely suppressed. The polymer cannot emerge from the boundary $x = 0$ with a positive slope. Thus the appropriate boundary conditions for equation (2) are

$$Z(x, u; x_0, u_0; 0) = \delta(x - x_0)\delta(u - u_0) \tag{3a}$$

$$Z(0, u; x_0, u_0; t) = 0 \qquad u > 0\,. \tag{3b}$$

For a free polymer, i.e. $V(x) = 0$, the solution of differential equation (2) with boundary condition (3*a*) in the unbounded x, t plane is given by [2]

$$Z_0(x, u; x_0, u_0; t) = 3^{1/2}(2\pi)^{-1}t^{-2}\exp\{-3t^{-3}[(x - x_0 - u_0t)^2$$

$$- t(x - x_0 - u_0t)(u - u_0) + \tfrac{1}{3}t^2(u - u_0)^2]\}\,. \tag{4}$$

In this paper the exact solution of equations (2) and (3) with $V(x) = 0$ is obtained in the semi-infinite geometry. A short-range pinning potential is then included within the framework of the 'necklace model' [6].

We begin by forming the Laplace transform of equations (2) and (3). This yields

$$\left[s + u\frac{\partial}{\partial x} - \frac{\partial^2}{\partial u^2} + V(x)\right]\tilde{Z}(x, u; x_0, u_0; s) = \delta(x - x_0)\delta(u - u_0) \tag{5a}$$

$$\tilde{Z}(0, u; x_0, u_0; s) = 0 \qquad u > 0 \tag{5b}$$

where

$$\tilde{Z}(x, u; x_0, u_0; s) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} Z(x, u; x_0, u_0; t)\,. \tag{5c}$$

In the force-free case $V(x) = 0$ it is convenient to expand $\tilde{Z}$ in eigenfunctions

$$\psi_{s,F}(u) = \psi_{s,-F}(-u) = F^{-1/6}\,\mathrm{Ai}(F^{1/3}u + F^{-2/3}s) \qquad F > 0 \tag{6a}$$

of Schrödinger's equation

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}u^2} + Fu + s\right)\psi_{s,F}(u) = 0 \tag{6b}$$

for a particle in a constant force field [7]. Here Ai is the standard Airy function [8, 9]. The $\psi_{s,F}$ have the orthonormality property

$$\int_{-\infty}^{\infty} \mathrm{d}u\, u\psi_{s,F}(-u)\psi_{s,F'}(-u) = \frac{F}{|F|}\delta(F - F') \tag{7a}$$

which follows from (6) and the Hermiticity of the operator $u^{-1}(-\mathrm{d}^2/\mathrm{d}u^2 + s)$ with respect to the scalar product $(f|g) = \int_{-\infty}^{\infty} \mathrm{d}u\, uf^*(u)g(u)$. The corresponding closure relation has the form

$$\int_0^\infty \mathrm{d}F\,[\psi_{s,F}(-u)\psi_{s,F}(-u') - \psi_{s,F}(u)\psi_{s,F}(u')] = u^{-1}\delta(u - u')\,. \tag{7b}$$

From equations (6) and (7*b*) one sees that differential equation (5*a*) has the particular solution

$$\tilde{Z}_0(x, u; x_0, u_0; s) = \int_0^\infty \mathrm{d}F\,[\theta(x - x_0)\mathrm{e}^{-F(x-x_0)}\psi_{s,F}(-u)\psi_{s,F}(-u_0)$$

$$+ \theta(x_0 - x)\mathrm{e}^{-F(x_0-x)}\psi_{s,F}(u)\psi_{s,F}(u_0)]\,. \tag{8}$$

This solution, which clearly vanishes in the limit $x \to \pm\infty$, represents the partition function for the polymer in the unbounded x, t plane and is thus the Laplace transform of $Z_0(x, u; x_0, u_0; t)$ in equation (4). The latter conclusion has been checked by numerical integration.

To satisfy the half-space boundary condition (5*b*), one must add to $\tilde{Z}_0$ an appropriate solution $\tilde{Z}_1$ of the homogeneous form of (5*a*). Both $e^{-Fx}\psi_{s,F}(-u)$ and $e^{Fx}\psi_{s,F}(u)$ satisfy the homogeneous differential equation, but the latter diverges for $x \to \infty$. Thus $\tilde{Z}_1$ is given by

$$\tilde{Z}_1(x, u; x_0, u_0; s) = \int_0^\infty dF\, w_F(x_0, u_0; s) e^{-Fx} \psi_{s,F}(-u) \tag{9}$$

with the function $w_F(x_0, u_0; s)$ still to be determined.

To impose boundary condition (5*b*), which only applies for $u > 0$, we make use of a remarkable set of functions $\phi_{s,F}(u)$ that have the biorthogonality property

$$\int_0^\infty du\, u \phi_{s,F}(-u) \psi_{s,F'}(-u) = \delta(F - F') \qquad F, F' > 0 \tag{10a}$$

on the semi-infinite interval $u > 0$ and satisfy

$$\phi_{s,F}(u) = 0 \qquad u > 0. \tag{10b}$$

Such a set was constructed by Marshall and Watson [10] in connection with the Fokker–Planck or Klein–Kramers equation [11–13]

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} - 2\alpha\frac{\partial}{\partial u} - \gamma\left(\frac{\partial}{\partial u}u + \frac{1}{m\beta}\frac{\partial^2}{\partial u^2}\right)\right] P(x, u; t) = 0 \tag{11}$$

for the distribution function $P(x, u; t)$ of Brownian particles moving with coefficient of friction γ in a medium with temperature $T = (k\beta)^{-1}$ and subject to a constant force $-2m\alpha$. Attempts to solve equation (11) in the semi-infinite geometry with the absorbing boundary condition $P(0, u; t) = 0$, $u > 0$ have a long history (see [13] for a summary). Marshall and Watson made a major advance and obtained the solution in terms of functions with properties analogous to (10).

In the limits $\alpha \to 0$, $\gamma = m\beta \to 0$, the Klein–Kramers differential equation (11) reduces to our differential equation (2) for Z, and the functions of Marshall and Watson take the form

$$\phi_{s,F}(u) = \psi_{s,F}(u) - \frac{1}{2\pi}\int_0^\infty \frac{dG}{F+G} \exp[-\tfrac{2}{3}s^{3/2}(F^{-1} + G^{-1})]\psi_{s,G}(-u). \tag{12}$$

Equation (12) implies the functional form $\phi_{s,F}(u) = F^{-1/6}\Phi(F^{1/3}u, F^{-2/3}s)$. The function $\Phi(U, S)$ is shown in figure 1. For $-1 \ll U < 0$, $\Phi(U, S) \approx \pi^{-1}\exp(-\frac{2}{3}S^{3/2})(-3U)^{1/2}$, and for $U > 0$, $\Phi(U, S)$ vanishes, as announced in equation (10*b*).

Knowing the explicit form (12) of the $\phi_{s,F}(u)$, one can readily construct the solution to differential equation (5*a*) for $\tilde{Z}$ with boundary condition (5*b*). It is given by

$$\tilde{Z} = \tilde{Z}_0 + \tilde{Z}_1 \tag{13a}$$

with $\tilde{Z}_0$ in (8) and

$$\tilde{Z}_1(x, u; x_0, u_0; s) = -\frac{1}{2\pi}\int_0^\infty dF \int_0^\infty dG\,(F+G)^{-1}$$
$$\times \exp\{-[Fx_0 + Gx + \tfrac{2}{3}s^{3/2}(F^{-1} + G^{-1})]\}\psi_{s,G}(-u)\psi_{s,F}(u_0). \tag{13b}$$

This can be checked as follows. Since $\tilde{Z}_0$ solves differential equation (5*a*) and $\tilde{Z}_1$ in equation (13*b*) has the form (9), $\tilde{Z}_0 + \tilde{Z}_1$ also satisfies the differential equation. To see that $\tilde{Z}_0 + \tilde{Z}_1$ satisfies boundary condition (5*b*), note that only the second term in $\tilde{Z}_0$ (see equation (8)) contributes in the limit $x \to 0$. For $x = 0, u > 0$ this term is cancelled by $\tilde{Z}_1$, since the right-hand side of (12) vanishes.

Calculating Z analytically for arbitrary t by inversion of its Laplace transform $\tilde{Z}$ in equations (8) and (13) does not appear to be feasible. However, the asymptotic form of Z for large t can be obtained analytically from the behaviour of $\tilde{Z}$ for small s. From (8) and (13) one finds that $\tilde{Z}$ and $\partial\tilde{Z}/\partial s$ remain finite in the limit $s \to 0$ and that $\partial^2\tilde{Z}/\partial s^2$ diverges as $s^{-1/2}$. The divergence stems from the factor $(-1/2)s^{-1/2}(F^{-1} + G^{-1})$ introduced in the integrand of equation (13*b*) (along with other contributions) by differentiating twice. The $s^{-1/2}$ behaviour corresponds via (5*c*) to the long-time behaviour $Z \sim t^{-5/2}$. Specifically

$$\pi^{1/2} \lim_{t\to\infty} t^{5/2} Z(x, u; x_0, u_0; t) = \lim_{s\to 0} s^{1/2} \frac{\partial^2}{\partial s^2} \tilde{Z}(x, u; x_0, u_0; s) = J(x, u) J(x_0, -u_0) \tag{14a}$$

where

$$J(x, u) = \frac{1}{2\pi^{1/2}} \int_0^\infty \mathrm{d}F\, F^{-7/6} [\mathrm{e}^{-Fx} \operatorname{Ai}(-F^{1/3}u) - \operatorname{Ai}(0)]\,. \tag{14b}$$

Evaluating the integral in (14*b*) and substituting the result in (14*a*) yields the asymptotic expression for large t

$$Z(x, u; x_0, u_0; t) \approx 4 \times 3^{2/3} \pi^{1/2} t^{-5/2} (x x_0)^{1/6} H(u x^{-1/3}) H(-u_0 x_0^{-1/3}) \tag{15a}$$

$$H(y) = \frac{M(-\frac{1}{6}, \frac{2}{3}, -\frac{1}{9}y^3)}{\Gamma(\frac{1}{6})\Gamma(\frac{2}{3})} + \frac{y}{9^{1/3}} \frac{M(\frac{1}{6}, \frac{4}{3}, -\frac{1}{9}y^3)}{\Gamma(-\frac{1}{6})\Gamma(\frac{4}{3})} \tag{15b}$$

where $M(a, b, x)$ is Kummer's confluent hypergeometric function [8]. It is simple to verify that equation (15) does indeed satisfy differential equation (2) in the large-t limit.

The function $H(y)$ is positive and decreases monotonically with increasing y. From the asymptotic forms [8]

$$H(y) \sim \begin{cases} \text{constant} \times y^{-5/2} \exp(-y^3/9) & y \to \infty \\ |y|^{1/2} & y \to -\infty \end{cases} \tag{16}$$

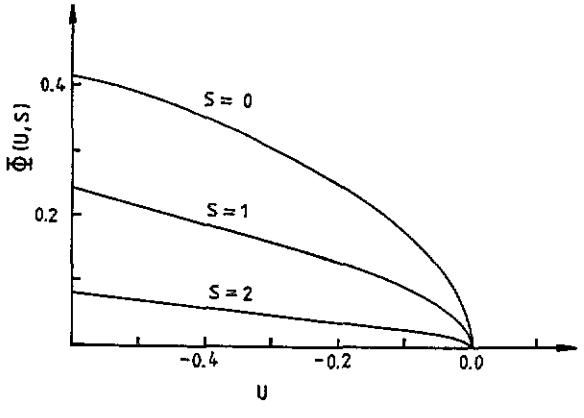

Figure 1. The function $\Phi(U, S)$ defined below equation (12).

one sees that the boundary condition (3*b*) is indeed satisfied by (15). Equation (15) is in complete agreement with the result $Z \sim t^{-5/2}x^{1/6}H(ux^{-1/3})$, obtained with semi-numerical approaches in [1, 2].

The adsorption or pinning transition of an infinitely long polymer in the presence of a short-range potential $V(x)$ attracting it to the boundary will now be considered, as in [1, 2], within the framework of the necklace model [6]. The polymer is built up of segments (beads of the necklace) that leave the boundary with zero slope and return to the boundary with zero slope. (The approach to the boundary is tangential since discontinuities in slope cost an infinite energy.) The relevant quantity for determining the order of the transition is the statistical weight $Z(a, 0; a, 0; t)$ of the bead, where a is a microscopic distance corresponding to the range of a contact potential. The phase transition in the necklace model [6] is first-order if the statistical weight of the bead has the asymptotic form $t^{-\psi}$ with $\psi > 2$ and second order for $1 < \psi < 2$. From equation (15) $\psi = \frac{5}{2}$, so that the polymer adsorption transition is first order.

The results of this letter are also applicable to two polymers with non-zero bending energy, fluctuating without overhangs in the unbounded x, t plane and interacting via a short-range attractive potential $V(x_1 - x_2)$ with a hard core, ensuring $x_1 > x_2$. The introduction of relative and centre-of-mass coordinates $x = x_1 - x_2$, $X = \frac{1}{2}(x_1 + x_2)$ reduces the two-polymer system to a single polymer in the half space $x > 0$. Thus the binding–unbinding transition of the two polymers is also first order.

We note a connection between the polymer partition function and the probabilities associated with the crossing of a line by the integral of a Brownian curve. Sinai [14] has analysed a discrete model with random variables Δu_t, $t = 1, 2, 3, \ldots$ that take the values ± 1 with equal probability. Thus $u_t = \Delta u_1 + \Delta u_2 + \cdots + \Delta u_t$ corresponds to a Brownian curve and $x_t = u_1 + u_2 + \cdots + u_t$ to the integral of a Brownian curve. He proved several theorems associated with the first crossing of the line $x = 0$ by x_t and showed that the probability that $x_{t'} \geqslant 0$ for all $t' = 1, 2, \ldots, t$ decays asymptotically as $t^{-1/4}$.

In our continuum polymer model $u(t)$ also corresponds to a Brownian curve and $x(t)$ to its integral. One expects the discretization to be irrelevant in the long-time limit, and it will now be shown that the $t^{-1/4}$ law also follows from the statistical weight $Z(x, u; x_0, u_0; s)$ for the polymer given in equations (8) and (13).

Since polymer configurations that intersect the boundary $x = 0$ with non-zero slope at t' only contribute to $Z(x, u; x_0, u_0; t)$ for $t < t'$, the 'survival probability'

$$q(x_0, u_0; t) = \int_0^\infty \mathrm{d}x \int_{-\infty}^\infty \mathrm{d}u\, Z(x, u; x_0, u_0; t) \tag{17}$$

also represents the probability that the integral $x(t)$ of a Brownian curve beginning at x_0, u_0 has not crossed the line $x = 0$ in a time t. From equation (2)

$$\frac{\partial}{\partial t} q(x_0, u_0; t) = -p(x_0, u_0; t) = \int_{-\infty}^\infty \mathrm{d}u\, u Z(0, u; x_0, u_0; t) \tag{18}$$

where $p(x_0, u_0; t)$ is the first passage time density.

Substituting (8) and (13) into (17) and using (6), (18) and the relation $\int_{-\infty}^\infty \mathrm{d}z\ \mathrm{Ai}(z) = 1$, one obtains

$$1 - s\tilde{q}(x_0, u_0; s) = \tilde{p}(x_0, u_0; s)$$

$$= s \int_0^\infty \mathrm{d}F\, F^{-5/3} \exp^{-Fx_0} \mathrm{Ai}(F^{1/3}u_0 + F^{-2/3}s) \left[1 + \frac{1}{4\pi^{1/2}} \Gamma(-\tfrac{1}{2}, \tfrac{2}{3}F^{-1}s^{3/2})\right] \tag{19}$$

for the Laplace transforms of $q(x_0, u_0; t)$ and $p(x_0, u_0; t)$. Here $\Gamma(\alpha, x)$ is the incomplete gamma function [8,9]. Analysing equation (19) for small s, one finds $\tilde{p}(x_0, u_0; 0) = 1$, meaning that the total probability $\int_0^\infty dt\, p(x_0, u_0; t)$ that the polymer intersects the boundary with positive slope is 1 or, equivalently, that the survival probability $q(x_0, u_0; t)$ vanishes in the limit $t \to \infty$. The quantity $\partial\tilde{p}/\partial s$ diverges as $s^{-3/4}$. Specifically

$$\lim_{s\to 0} s^{3/4}\frac{\partial}{\partial s}\tilde{p}(x_0, u_0; s) = -\frac{1}{4}3^{5/6}(2\pi)^{1/2}x_0^{1/6}H(-u_0x_0^{-1/3}) \tag{20}$$

in terms of the function $H(y)$ of equation (15*b*). This corresponds via (5*c*) and (18) to the long-time behaviour

$$q(x_0, u_0; t) \approx 4tp(x_0, u_0; t) \approx 3^{5/6}(2\pi)^{1/2}\Gamma(\tfrac{3}{4})^{-1}t^{-1/4}x^{1/6}H(-u_0x_0^{-1/3})\,. \tag{21}$$

Thus, in the polymer model the survival probability decays asymptotically as $t^{-1/4}$, and the first passage time density as $t^{-5/4}$, as in Sinai's discrete model [14].

Finally we note that the adsorbtion transition of a self-avoiding walk or polymer in two dimensions, with overhangs included but with zero bending energy, is second order [15]. The bending energy plays a role on length scales smaller than the persistance length but is expected to be an irrelevant variable in the adsorption transition [1]. The omission of polymer configurations with overhangs is a reasonable approximation in the adsorbed phase. However, it is clearly a relevant modification in the adsorption transition since it leads, as we have seen, to a first-order transition.

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