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Path-integral theory of an axially confined worm-like chain

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Abstract

A path-integral formulation is developed for the thermodynamic properties of a worm-like chain moving on a surface and laterally confined by a harmonic potential. The free energy of the chain is calculated as a function of its length and boundary conditions at each end. Distribution functions for chain displacements can be constructed by utilizing the Markov property as a function of displacement $\phi(s)$ and its derivative $\mathrm{d}\phi(s)/\mathrm{d}s$ along the path. These quantities are also calculated in the presence of pinning sites which impose fixed positive or negative displacements, foreshadowing their application to a model for the regulation of striated muscle.

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1. Introduction

The simplest worm-like-chain model of a polymer filament supposes that the polymer can be treated as a continuous inextensible one-dimensional chain with a finite bending modulus (Kratky and Porod 1949, Doi and Edwards 1988). This model has been applied to the force-extension curve of a single biopolymer filament (Marko and Siggia 1995, Tskhovrebova *et al* 1997, Wang *et al* 1997), which may show enthalpic and entropic contributions. Path-integral theories for finite-temperature equilibrium properties of worm-like chains are complicated by the fact that bending energy is proportional to the square of the *second* path derivative of chain position, and specialized methods of calculation have been invented for the purpose (Papadopoulos and Thomchick 1977, Kleinert 1986).

This paper considers the problem of a worm-like chain moving on a flat surface and confined to the vicinity of a straight line on that surface by a harmonic potential. This problem is motivated by a well known mechanism for the regulation of muscle contraction, discussed briefly at the end of this paper. Let $\phi(s)$ be the lateral displacement of the chain at distance s along the chain (figure 1). The corresponding potential energy functional is assumed to be

$$E[\phi(s)] = \int_0^L \left(\frac{\kappa}{2}\phi''(s)^2 + \frac{\alpha}{2}\phi(s)^2\right)\mathrm{d}s \tag{1.1}$$

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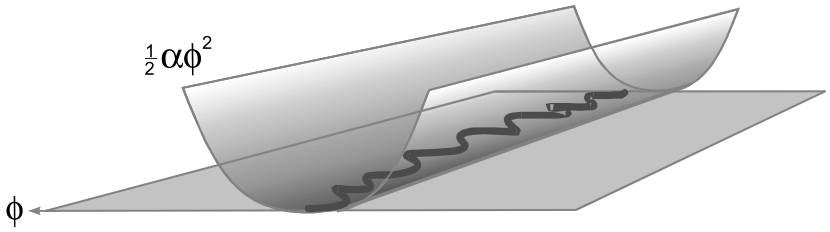

Figure 1. Schematic drawing of a worm-like chain on a surface and laterally confined near the zero of the axial potential $\alpha\phi^2/2$ as shown, with different displacements ϕ in the lateral direction at each point of the chain.

where primes denote differentiation with respect to s and κ is the shear elastic constant per unit length of chain. The bending energy per unit length is generally proportional to $|\boldsymbol{r}''(s)|^2$, which reduces to the first term of the integrand for slowly varying displacements such that[1] $|\phi'(s)| \ll 1$. The second term tends to confine the chain to the vicinity of the straight line $\phi(s) = 0$, so that the energy of the resting chain is zero. As the chain is assumed to be inextensible, there is no stretching-energy term.

The partition function and hence the free energy of the chain described by (1.1) is calculated for fixed boundary conditions at each end. The method of calculation gives the probability distribution of displacements at any site on the chain, also the joint distribution of displacements at any number of sites. To apply this model to muscle regulation, formulae are also derived for the partition function in the presence of an arbitrary distribution of n pinning sites where the displacement of the chain is fixed. At the molecular level, pinning can be achieved in various ways considered in the concluding discussion. A key parameter for describing the influence of pinning sites is the persistence length for the confined chain, which is found to be $1/\xi$ where

$$\xi^4 \equiv \alpha/4\kappa. \tag{1.2}$$

With the above application in mind, recursive formulae are established for the free energy of the pinned chain and the distribution of displacements near pinning sites, and illustrated for the case $n = 2$.

The path-integral must be calculated by dividing the chain into repeating cells, and defining a measure which 'regularizes' the integral to give a finite result in the limit of zero cell length. This continuum limit appears to be appropriate for describing thermally excited long-wavelength distortions of a real polymeric chain, but the consequences should be recognized before proceeding further. Firstly, the law of equipartition of energy and associated high-temperature properties obtained from the classical partition function requires a finite number of degrees of freedom, which should be the total number of atoms in the chain; this statement appears to require the existence of a unit cell (the monomer) with an atomic basis. In the continuum limit these degrees of freedom are not thermally excited, but a fully quantum-mechanical treatment seems inappropriate.

The calculation of thermodynamic properties from the partition function is normally indifferent to any multiplicative factor, which cancels out of the Boltzmann average. A weighting factor must be included for each cell of the discretized chain to regularize the path integral. In this case the weighting factor is temperature-dependent, and the expression $-\mathrm{d}\ln Z/\mathrm{d}\beta$ for internal energy, where $\beta = 1/k_BT$ (k_B is Boltzmann's constant and T is the

[1] In terms of coordinates $x(s)$, $y(s)$ parallel and perpendicular to the line of confinement, $|\boldsymbol{r}''(s)|^2 \equiv x''(s)^2 + y''(s)^2 = y''(s)^2/(1 - y'(s)^2)$ since $\mathrm{d}s^2 = \mathrm{d}x^2 + \mathrm{d}y^2$. In the main text, $y(s)$ is replaced by $\phi(s)$ and other meanings are given to the symbols x, y.

absolute temperature), is correct only if the weighting factor is held constant when taking the derivative. For the energy function (1.1), equipartition of energy is restored by multiplying the 'path-integral' partition function by a factor $\beta^{-N/2}$, where N is the total number of degrees of freedom in the chain, giving the missing internal energy $Nk_BT/2$. Nevertheless, the 'path' partition function will be used to calculate changes in the number of configurations associated when the chain is pinned, and hence the change in chain free energy including the entropic term.

The classical partition function of a confined worm-like chain pinning is formally analogous to the path-integral for Hamiltonian action of a particle with a quasi-kinetic energy proportional to (acceleration)^2 rather than (velocity)^2 and moving in a harmonic potential (Kleinert 1986). The integration over all chain paths with specified end conditions is replaced by integrating over all trajectories of the particle in time (Feynman and Hibbs 1965). The pinned chain can be viewed as a special case of a chain moving in an external position-dependent potential acting only at pinning sites, analogous to a particle moving in a time-dependent (and pulsatile) external potential. These problems can be solved by dividing the chain/trajectory into segments in which the chain/particle moves without external constraints.

2. The confined chain

The partition function of a confined chain of length L may be written as the path integral

$$Z_{ab} = \int_a^b \exp(-\beta E[\phi(s)])\, D\phi(s) \tag{2.1}$$

($\beta = 1/k_BT$, k_B is Boltzmann's constant, T is the absolute temperature) which averages over all possible displacements of the chain between fixed end-points a and b. Following Feynman's method, we first obtain the path of minimum energy E_0 between these end-points, giving a factor $\exp(-\beta E_0)$ which can be taken outside the path integral; the remaining factor W is determined by the number of thermally activated paths at higher energy and requires the path integral to be defined via a discrete representation of the chain.

The path of minimum energy satisfies the extremal condition

$$\begin{aligned}\delta E/\kappa &= \int_0^L \left(\phi''\delta\phi'' + 4\xi^4\phi\delta\phi\right) \mathrm{d}s \\ &= \left[\phi''\delta\phi' - \phi'''\delta\phi\right]_a^b + \int_0^L \left(\phi^{(4)} + 4\xi^4\phi\right)\delta\phi\, \mathrm{d}s = 0\end{aligned} \tag{2.2}$$

so

$$\left(\frac{\mathrm{d}^4}{\mathrm{d}s^4} + 4\xi^4\right)\phi(s) = 0 \tag{2.3}$$

if $\phi(s)$ and its first derivative are fixed at the ends. Most of the ensuing complication stems from these four boundary conditions, which arise from the form of the bending energy. The functions

$$\begin{aligned} u_1(x) &= \sinh x \sin x \qquad & u_2(x) &= \cosh x \sin x \\ u_3(x) &= \sinh x \cos x \qquad & u_4(x) &= \cosh x \cos x \end{aligned} \tag{2.4}$$

with $x = \xi s$ are independent solutions of (2.3). The extremal path can be expressed in terms of these functions as

$$\phi_0(s) = \sum_{k=1}^{4} c_k u_k(\xi s) \tag{2.5}$$

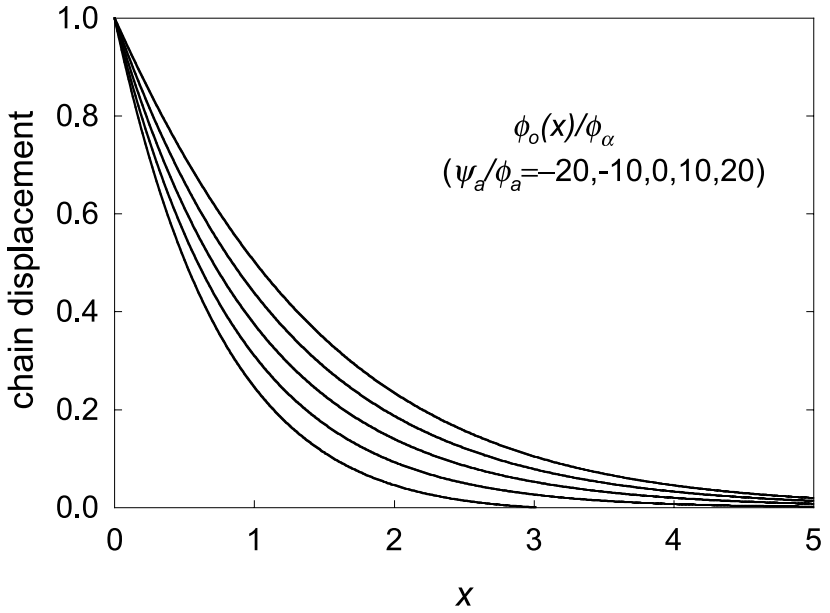

Figure 2. The most probable displacement $\phi_0(x)$ of a long chain near one end ($x = 0$) subject to fixed values ϕ_a, ψ_a of displacement and its path derivative respectively at the end, as a function of the reduced path length $x = \xi s$. From equation (2.5) and appendix A, the predicted function for a chain of length $L \gg 1/\xi$ is $\phi_0(x) = \exp(-x)(\sin x + \cos x)\phi_a + \exp(-x)\sin(x)\psi_a$, with 'overdamped' behaviour which is relatively insensitive to the ratio ψ_a/ϕ_a. Similar functions are predicted for the dynamical behaviour of a damped chain (Wiggins *et al* 1998).

where the coefficients are determined by the boundary values. Explicit expressions for the c_k are given in appendix A. The minimum energy E_0 can be obtained from (1.1), since integrations by parts as before gives

$$E_0 = \frac{\kappa}{2}\left[\phi_0''(s)\phi_0'(s) - \phi_0'''(s)\phi_0(s)\right]_0^L \tag{2.6}$$

in terms of boundary values only. However, equation (2.5) is required to express the higher derivatives in terms of $\phi_a, \phi_a', \phi_b, \phi_b'$. It is convenient to use scaled derivatives $\psi_a = \phi_a'/\xi$, $\psi_b = \phi_b'/\xi$ at the boundaries. Thus

$$E_0 = \kappa\xi^3\big[A_{11}(\phi_a^2 + \phi_b^2) + 2A_{12}(\phi_a\psi_a - \phi_b\psi_b) + A_{22}(\psi_a^2 + \psi_b^2) + B_{11}\phi_a\phi_b + B_{12}(\phi_a\psi_b - \psi_a\phi_b) + B_{22}\psi_a\psi_b\big] \tag{2.7}$$

or in terms of 2×2 matrices,

$$E_0 = \kappa\xi^3\left\{\Phi_a \boldsymbol{A}\Phi_a + \Phi_b \boldsymbol{A}^{\mathrm{S}}\Phi_b + \Phi_a \boldsymbol{B}\Phi_b\right\} \tag{2.8}$$

where

$$\boldsymbol{\Phi}_a = \begin{pmatrix} \phi_a \\ \psi_a \end{pmatrix} \qquad \boldsymbol{\Phi}_b = \begin{pmatrix} \phi_b \\ \psi_b \end{pmatrix} \tag{2.9}$$

and $\boldsymbol{A}$ is symmetric, $\boldsymbol{B}$ antisymmetric. $\boldsymbol{A}^{\mathrm{S}}$ is the skew complement of $\boldsymbol{A}$, whose off-diagonal elements are reversed in sign. In passing, note that $\boldsymbol{B}^{\mathrm{S}}$ is the transpose of $\boldsymbol{B}$. The coefficients

are functions of the scaled chain length $X = \xi L$, namely

$$\begin{aligned} A_{11} &= 2\frac{\sinh X \cosh X + \sin X \cos X}{d(X)} & B_{11} &= -4\frac{\sinh X \cos X + \cosh X \sin X}{d(X)} \\ A_{12} &= \frac{\sinh^2 X + \sin^2 X}{d(X)} & B_{12} &= 4\frac{\sinh X \sin X}{d(X)} \\ A_{22} &= \frac{\sinh X \cosh X - \sin X \cos X}{d(X)} & B_{22} &= 2\frac{\cosh X \sin X - \sinh X \cos X}{d(X)} \end{aligned} \tag{2.10}$$

where $d(X) = \sinh^2 X - \sin^2 X$. For $X \gg 1$, the elements of $\boldsymbol{A}$ tend to finite positive values while those of $\boldsymbol{B}$ tend to zero, so that the boundary conditions at each end act independently on the chain. The path of minimum energy then tends to zero displacement in the interior, with independent matching to the boundary conditions at each end. Figure 2 shows that this behaviour depends on the boundary value of the derivative; the damped oscillatory decay is characteristic of the confined bending chain.

Asymptotic forms as $X \to 0$ can also be obtained. In this limit the leading term in the energy is independent of ξ, and can be interpreted either as the behaviour of a very short chain at finite ξ or an unconfined chain ($\xi = 0$) of any length. The minimal energy of such a chain is

$$E_0 = \frac{2\kappa}{L}\left\{3\left(\frac{\phi_b - \phi_a}{L}\right)^2 - 3\frac{\phi_b - \phi_a}{L}(\phi'_a + \phi'_b) + \phi'^2_a + \phi'_a\phi'_b + \phi'^2_b\right\} \tag{2.11}$$

which arises from bending only, and the corresponding path is the cubic polynomial

$$\phi_0(s) = \phi_a + \phi'_a s + \left(3\frac{\phi_b - \phi_a}{L} - 2\phi'_a - \phi'_b\right)\frac{s^2}{L} + \left(\phi'_a + \phi'_b - 2\frac{\phi_b - \phi_a}{L}\right)\frac{s^3}{L^2} \tag{2.12}$$

which describes the bending of a loaded cantilever (Southwell 1936). Note that when $\phi'_a = \phi'_b = (\phi_b - \phi_a)/L$, the minimal path is a straight line and $E_0 = 0$.

The contribution of thermally activated chain configurations to the partition function is given by a factor of the same form as (2.1), where the chain path is replaced by its fluctuating part $\delta\phi(s)$; this is true for any quadratic energy functional (Feynman and Hibbs 1965). For this problem, $\delta\phi(s) = \delta\phi'(s) = 0$ at $s = 0$ and L. To define the path integral, the chain must now be discretized to convert (2.1) into a multiple integral of finite dimensions: at this point it is sufficient to consider the simpler case of the unconstrained chain ($\alpha = 0$). Once the path integral is regularized, the solution for the harmonically constrained chain can be obtained by Feynman's method.

Let the chain be divided into N cells each of length $\varepsilon \equiv L/N$, and assign fluctuating displacements $\delta\phi_n$ to sites $s_n = n\varepsilon$ for $n = (0, N)$. At the ends, $\delta\phi_0 = \delta\phi_N = 0$. Discrete analogues of zero displacement derivatives at each end are incorporated by allowing two more sites $n = -1$, $N+1$ with zero displacements. Dropping the 'δ' prefix, the discretized fluctuation energy is now

$$E_N = \frac{\kappa}{2\varepsilon^3}\sum_{n=0}^{N}\left\{(\phi_{n-1} - 2\phi_n + \phi_{n+1})^2 + 4\varepsilon^4\xi^4\phi_n^2\right\} \tag{2.13}$$

or $(\kappa/2\varepsilon^3)\Phi_{N-1}\boldsymbol{M}_{N-1}\Phi_{N-1}$ in terms of a displacement vector $(\phi_1, \ldots, \phi_{N-1})$ and the matrix

$$\boldsymbol{M}_N = \begin{pmatrix} 6+\lambda & -4 & 1 & & & & 0 \\ -4 & 6+\lambda & -4 & 1 & & & \\ 1 & -4 & 6+\lambda & -4 & 1 & & \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \\ & & \cdot & \cdot & \cdot & \cdot & \cdot \\ & & & \cdot & \cdot & \cdot & \cdot \\ 0 & & & & 1 & -4 & 6+\lambda \end{pmatrix}_N \tag{2.14}$$

with $\lambda = 4(\varepsilon\xi)^4$. The path differential is defined as the limit for large N of the multiple integral

$$D_N\phi \equiv \varepsilon^{-\mu} \int \prod_{n=1}^{N-1} \frac{\mathrm{d}\phi_n}{C\varepsilon^{\nu}} \tag{2.15}$$

so that the fluctuating factor for equation (2.2) is (Doi and Edwards 1988)

$$\begin{aligned} W_N &= \int D_N\phi \exp\left(-\frac{\beta\kappa}{2\varepsilon^3}\Phi_{N-1}\boldsymbol{M}_{N-1}\Phi_{N-1}\right) \\ &= \varepsilon^{-\mu}\left(\frac{2\varepsilon^{3-2\nu}}{\beta\kappa C^2}\right)^{(N-1)/2}\left(\frac{\pi^{N-1}}{|\boldsymbol{M}_{N-1}|}\right)^{1/2} \end{aligned} \tag{2.16}$$

requiring the determinant of (2.14).

For the unconfined chain ($\lambda = 0$), this determinant can be evaluated as (see appendix B)

$$|\boldsymbol{M}_{N-1}| = N^4/12 + \mathrm{O}(N^3). \tag{2.17}$$

The path-integral remains finite in the limit $\varepsilon \to 0$, $N \to \infty$ at fixed L iff

$$\mu = 2 \qquad \nu = \tfrac{3}{2} \qquad C = (2\pi/\beta\kappa)^{1/2} \tag{2.18}$$

giving $W = 2\sqrt{3}/L^2$ in the limit. This 'regularization' of the path integral should remain valid for the confined chain, as expected when adding a potential term (Brush 1961).

The third and final step is to calculate W for the confined chain, using the same regularization. Various analytic methods are available (Kleinert 1995, Grosche and Steiner 1998), but they usually revert to some form of eigenvalue problem. An alternative approach is to seek a composition law for the partition function by joining two chains end to end, as used by Feynman for particle trajectories. Figure 3 shows how this can be done for discretized chains so that their displacements at the join define a common boundary value of the path derivative. If the partition functions of the separate chains are

$$\begin{aligned} Z_M(\phi_{-1}, \phi_0, \phi_M, \phi_{M+1}) &= \int D_M\phi \exp(-\beta E_M[\phi]) \\ Z_N(\theta_{-1}, \theta_0, \theta_N, \theta_{N+1}) &= \int D_N\theta \exp(-\beta E_N[\theta]) \end{aligned} \tag{2.19}$$

where $\phi_M \equiv \theta_{-1}$, $\phi_{M+1} \equiv \theta_0$, the partition function of the combined chain is

$$\begin{aligned} Z_{M+N+1}(\phi_{-1}, \phi_0, \theta_N, \theta_{N+1}) &= \int D_{M+N+1}(\phi, \theta) \exp(-\beta\{E_M[\phi] + E_N[\theta]\}) \\ &= \varepsilon^{-2}\int \prod_{m=1}^{M-1} \frac{\mathrm{d}\phi_m}{C\varepsilon^{3/2}} \int \frac{\mathrm{d}\phi_M}{C\varepsilon^{3/2}} \int \frac{\mathrm{d}\theta_0}{C\varepsilon^{3/2}} \int \prod_{n=1}^{N-1} \frac{\mathrm{d}\theta_n}{C\varepsilon^{3/2}} \exp(-\beta\{E_M[\phi] + E_N[\theta]\}) \\ &= \frac{1}{C^2\varepsilon}\iint \mathrm{d}\phi_M\, \mathrm{d}\theta_0\, Z_M(\phi_{-1}, \phi_0, \phi_M, \theta_0) Z_N(\phi_M, \theta_0, \theta_N, \theta_{N+1}). \end{aligned}$$

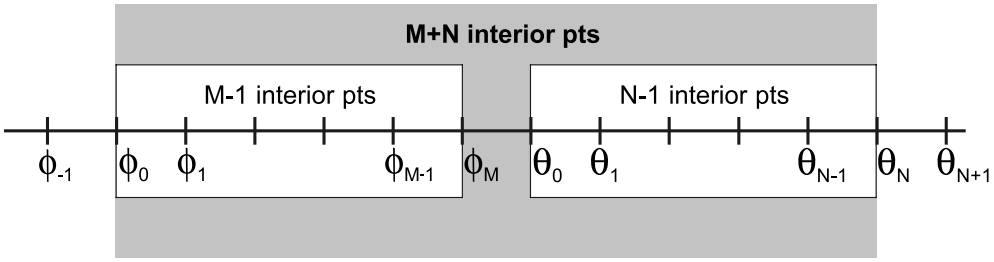

Figure 3. The combination of two chains showing their discrete representations containing M and N cells. Displacements external to these chains are defined at each end and their join so that boundary values of displacement derivative along the path are defined in the limit of zero cell size.

The limit $\varepsilon \to 0$ can be taken after replacing one integration by an integral over the derivative $\phi'_c \approx (\theta_0 - \phi_M)/\varepsilon$, which gives the desired composition law,

$$Z(\phi_a, \phi'_a; \phi_b\phi'_b) = \frac{1}{C^2}\iint \mathrm{d}\phi_c\, \mathrm{d}\phi'_c\, Z(\phi_a, \phi'_a; \phi_c\phi'_c)\, Z(\phi_c, \phi'_c; \phi_b\phi'_b). \quad (2.20)$$

This result provides the basis for constructing partition functions and displacement distributions, with or without pinning sites.

Using condensed notation and setting, for example $Z_{ab} = W(X_{ab})\exp(-\beta E_{ab})$ where $X_{ab} = \xi(s_b - s_a)$, equation (2.20) generates a similar identity

$$\frac{W(X+Y)}{W(X)W(Y)} = \frac{\xi}{C^2}\int \mathrm{d}^2\Phi_c \exp(-\beta\{E_{ac} + E_{cb} - E_{ab}\}) \quad (2.21)$$

for the fluctuation factors, using scaled path derivatives and the vector (2.9). The exponent can be constructed from the basic energy formula (2.8), showing that the boundary vector has a bi-variate Gaussian distribution. The standard integral

$$I = \int \mathrm{d}^2 u \exp(-\{\boldsymbol{u}\boldsymbol{H}\boldsymbol{u} + 2\boldsymbol{u}\cdot\boldsymbol{b}\}) = \frac{\pi}{|\boldsymbol{H}|^{1/2}}\exp(\boldsymbol{b}\boldsymbol{H}^{-1}\boldsymbol{b}) \quad (2.22)$$

is repeatedly required. In this case,

$$\boldsymbol{H}(X,Y) = \boldsymbol{A}^{\mathrm{S}}(X) + \boldsymbol{A}(Y) \qquad \boldsymbol{b} = \tfrac{1}{2}(\boldsymbol{B}^{\mathrm{S}}(X)\boldsymbol{u}_a + \boldsymbol{B}(Y)\boldsymbol{u}_b) \quad (2.23)$$

and

$$\boldsymbol{u}_a = \sqrt{\beta\kappa\xi^3}\,\Phi_a \qquad \boldsymbol{u}_b = \sqrt{\beta\kappa\xi^3}\,\Phi_b \quad (2.24)$$

are dimensionless displacement vectors. The identities

$$\begin{aligned}
&\tfrac{1}{4}\boldsymbol{B}(X)\boldsymbol{H}(X,Y)^{-1}\boldsymbol{B}^{\mathrm{S}}(Y) \equiv \boldsymbol{A}(X) - \boldsymbol{A}(X+Y)\\
&\tfrac{1}{4}\boldsymbol{B}^{\mathrm{S}}(Y)\boldsymbol{H}(X,Y)^{-1}\boldsymbol{B}(Y) \equiv \boldsymbol{A}^{\mathrm{S}}(Y) - \boldsymbol{A}^{\mathrm{S}}(X+Y)\\
&\tfrac{1}{2}\boldsymbol{B}(X)\boldsymbol{H}(X,Y)^{-1}\boldsymbol{B}(Y) \equiv -\boldsymbol{B}(X+Y)
\end{aligned} \quad (2.25)$$

are also helpful. In this way one finds the composition relation

$$\frac{W(X)W(Y)}{W(X+Y)} = \frac{\beta\kappa\xi^2C^2}{\pi}\,|\boldsymbol{H}(X,Y)|^{1/2} \quad (2.26)$$

which can be solved for $W(X)$ by developing a differential equation. The solution is

$$W(X) = \frac{\sqrt{2}\beta\kappa\xi^2 C^2/\pi}{\sqrt{\sinh^2 X - \sin^2 X}} \tag{2.27}$$

where the numerator is $2\sqrt{2}\xi^2$ on using (2.18) for C. The previous result $2\sqrt{3}/L^2$ is recovered when $X \equiv \xi L \ll 1$. In the opposite limit of a long chain, $W(X) \approx 4\sqrt{2}\xi^2 \exp(-\xi L)$.

The 'path' free energy of the chain with prescribed boundary conditions may be defined in the usual way as

$$F_{ab} \equiv -k_B T \ln Z_{ab} = E_{ab}(\phi_a, \phi'_a, \phi_b, \phi'_b) - k_B T \ln W(X_{ab}). \tag{2.28}$$

However, thermodynamic formulae $U_{ab} \equiv -\mathrm{d}(\ln Z_{ab})/\mathrm{d}\beta$ and $S_{ab} \equiv (U_{ab} - F_{ab})/T$ for internal energy and entropy are correct only if the (temperature-dependent) regularization constant C is held constant, and the substitution (2.18) made after taking the β-derivative. Thus $U_{ab} = E_{ab} - k_B T$, in which thermally excited degrees of freedom are missing. The second term is associated with fixed displacements at each end; on using periodic boundary conditions ($\Phi_a = \Phi_b$) and integrating the partition function over this vector, two extra degrees of freedom are supplied and the 'path' internal energy becomes the ground-state energy E_{ab}. This energy can be used as a reference for calculating changes in internal energy produced by pinning the chain. The same utilitarian interpretation also applies to the 'path' entropy, which is $k_B(\ln W(X_{ab}) - 1)$ for the chain with fixed ends or $k_B \ln W(X_{ab})$ with periodic boundary conditions.

3. Distributions of displacements

Under thermal-equilibrium conditions, the distribution of lateral displacements of the chain can be constructed using the methods of the last section. It is necessary to start with the joint distribution of displacement ϕ and its path derivative ϕ', which can be treated as independent variables. Let $P(\Phi_1)$ be the joint probability distribution of ϕ and the scaled derivative ψ at position s_1 on a chain of length L. Similar joint distributions $P(\Phi_1, \ldots, \Phi_n)$ can be defined for any number n of sites on the chain. Denoting the ends by a, b as before, repeated applications of the composition law (2.20), or in condensed form

$$Z_{ab} = \frac{\beta\kappa\xi}{2\pi} \int \mathrm{d}^2\Phi_1 \, Z_{a1} Z_{1b} \tag{3.1}$$

using (2.18) for C, allows all distributions to be written down, for example

$$\begin{aligned} P(\Phi_1) &= \frac{\beta\kappa\xi}{2\pi} \frac{Z_{a1}(\Phi_a, \Phi_1) Z_{1b}(\Phi_1, \Phi_b)}{Z_{ab}(\Phi_1, \Phi_b)} \\ P(\Phi_1, \Phi_2) &= \left(\frac{\beta\kappa\xi}{2\pi}\right)^2 \frac{Z_{a1}(\Phi_a, \Phi_1) Z_{12}(\Phi_1, \Phi_2) Z_{2b}(\Phi_2, \Phi_b)}{Z_{ab}(\Phi_1, \Phi_b)}. \end{aligned} \tag{3.2}$$

Equation (3.1) confirms that these distributions are normalized to unity. For a long chain ($\xi L \gg 1$), the one-site distribution at an interior site (several persistence lengths from either end) should be independent of the boundary displacements, and the two-site distribution should depend only on the separation s_{12} between the sites.

Explicit formulae are simplified by using the dimensionless displacement vector $\boldsymbol{u} = (\beta\kappa\xi^3)^{1/2}\Phi$ with components (u, v), so

$$Z_{ab} = W(X_{ab}) \exp(-[\boldsymbol{u}_a \boldsymbol{A}(X) \boldsymbol{u}_a + \boldsymbol{u}_a \boldsymbol{B}(X) \boldsymbol{u}_b + \boldsymbol{u}_b \boldsymbol{A}^{\mathrm{S}}(X) \boldsymbol{u}_b]). \tag{3.3}$$

At any interior point of a long chain, the one-site distribution with respect to $\boldsymbol{u}$ is

$$p(\boldsymbol{u}) = \frac{\sqrt{8}}{\pi}\exp(-(4u^2 + 2v^2)) \tag{3.4}$$

the product of Gaussian distributions in u and v with standard deviations of $1/\sqrt{8}$ and $\frac{1}{2}$, respectively. For two interior sites, the analogous joint distribution is

$$p(\boldsymbol{u}_1, \boldsymbol{u}_2) = \frac{\sqrt{8}}{\pi^2}|\boldsymbol{G}(x)|^{1/2}\exp(-(\boldsymbol{u}_1\boldsymbol{G}(x)\boldsymbol{u}_1 + \boldsymbol{u}_1\boldsymbol{B}(x)\boldsymbol{u}_2 + \boldsymbol{u}_2\boldsymbol{G}^{\mathrm{S}}(x)\boldsymbol{u}_2)) \tag{3.5}$$

where $x \equiv \xi s_{12}$ and $\boldsymbol{G}(x) \equiv \boldsymbol{H}(\infty, x)$ as in (2.23). With the aid of (2.25), it can be shown that $p(\boldsymbol{u}_1)$ is recovered on integrating over $\boldsymbol{u}_2$. When $x \to 0$, $p(\boldsymbol{u}_1, \boldsymbol{u}_2) \approx p(\boldsymbol{u}_1)\delta(\boldsymbol{u}_1 - \boldsymbol{u}_2)$ where $\delta(\boldsymbol{u})$ is a product of Dirac delta functions in u and v. The dependence on site distance is not very transparent, but when $x \gg 1$ the matrix $\boldsymbol{B}$ becomes vanishingly small and independent distributions are recovered, namely $p(\boldsymbol{u}_1, \boldsymbol{u}_2) \approx p(\boldsymbol{u}_1)p(\boldsymbol{u}_2)$.

The two-site distribution for displacements only is obtained from (3.5) by integrating over v_1, v_2. This produces another bi-variate Gaussian distribution for the dimensionless displacements u_1, u_2, with similar behaviour as a function of x. The same information is contained in the conditional distribution $p(u_2|u_1) \equiv p(u_1, u_2)/p(u_1)$, where $p(u) = (2/\sqrt{\pi})\exp(-4u^2)$ is the one-site distribution. Hence

$$p(u_2|u_1) = \left(\frac{C_1(x)}{\pi}\right)^{1/2}\exp\left(-C_1(x)\left(u_2 + \frac{C_2(x)}{C_1(x)}u_1\right)^2\right) \tag{3.6}$$

where

$$\begin{aligned} C_1 &= G_{11} - \frac{G_{22}(4G_{12}^2 + B_{12}^2) - 2B_{22}G_{12}B_{12}}{4G_{22}^2 - B_{22}^2} \\ 2C_2 &= B_{11} + \frac{8G_{22}G_{12}B_{12} - B_{22}(4G_{12}^2 + B_{12}^2)}{4G_{22}^2 - B_{22}^2} \end{aligned} \tag{3.7}$$

and the identity $C_1^2 - C_2^2 \equiv 4C_1$ ensures correct normalization. As a function of reduced separation x, the mean and variance of the distribution of u_2 are

$$\begin{aligned} \frac{\overline{u_2}(x|u_1)}{u_1} &\equiv R(x) = -\frac{C_2(x)}{C_1(x)} \\ \overline{u_2^2}(x|u_1) - (\overline{u_2}(x|u_1))^2 &\equiv S(x) = \frac{1}{2C_1(x)} \end{aligned} \tag{3.8}$$

starting from u_1 at $x = 0$. After some manipulation of symbols,

$$\begin{aligned} R(x) &= \exp(-x)(\cos x + \sin x) \\ S(x) &= \tfrac{1}{8}\{1 - \exp(-2x)(1 + \sin 2x)\}. \end{aligned} \tag{3.9}$$

The quantity R is also the cross-correlation function of the joint distribution. These universal functions of x are plotted in figure 4. As a function of u_2, the distribution (3.6) evolves from a delta function localized at u_1 when $x = 0$ to the symmetric one-site Gaussian distribution when $x \gg 1$, analogous to the Ornstein–Uhlenbeck solution of the Fokker–Planck equation for the time behaviour of a harmonically bound Brownian particle (Chandrasekhar 1943).

The composition law (3.1) can be viewed more generally as a form of the Chapman–Kolmogorov equation for stochastic processes (Gardner 1985), which implies that the transmission of probabilities down the chain is a Markov process in the two-dimensional vector

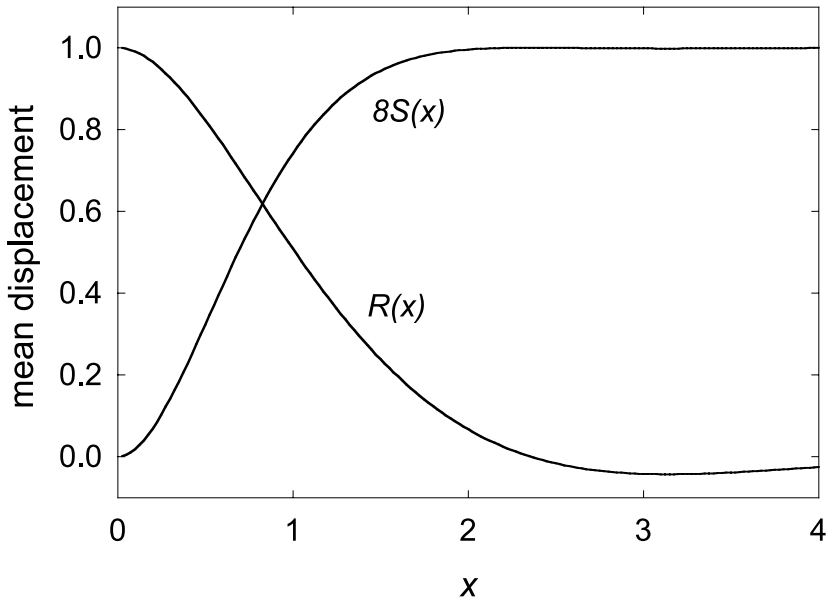

Figure 4. Mean chain displacement $R(x)$ from equation (3.9) at distance x (measured in units of $1/\xi$) from a point of known displacement, expressed as a ratio of the latter as in equation (3.8). $S(x)$ is the displacement variance at this point. When x increases above unity, memory of the imposed displacement is lost and the variance grows to its normal value of $\frac{1}{8}$. The results confirm that $1/\xi$ defines the persistence length of the confined chain.

$\boldsymbol{u}(s)$. If $p(1,\ldots,n)$ denotes a joint n-site distribution in these vectors, the corresponding form $Z_{ab} = \rho \int \mathrm{d}^2\boldsymbol{u}_1\, Z_{a1} Z_{1b}$ of (3.1), where $\rho = (2\pi\xi^2)^{-1}$, generates conditional distributions

$$\begin{aligned} p(3|12) &\equiv \frac{p(123)}{p(12)} = \frac{\rho^3 Z_{a1} Z_{12} Z_{23} Z_{3b}}{\rho^2 Z_{a1} Z_{12} Z_{2b}} = \rho \frac{Z_{23} Z_{3b}}{Z_{2b}} \\ p(3|2) &\equiv \frac{p(23)}{p(2)} = \frac{\rho^2 Z_{a2} Z_{23} Z_{3b}}{\rho Z_{a2} Z_{2b}} = \rho \frac{Z_{23} Z_{3b}}{Z_{2b}}. \end{aligned} \tag{3.10}$$

Thus $p(3|12) = p(3|2)$. In general, one can show that if (vectorial) displacements are given at n positions along the chain, the distribution of displacement at a site further ahead depends only on the displacement at the nearest preceding site, so

$$p(n+1|1,2,\ldots,n) = p(n+1|n) \tag{3.11}$$

if the sites are indexed by path position. An equivalent statement must hold if all given displacements are further down the chain, since the energy functional is invariant if path lengths are measured from the other end. If displacements are specified on both sides of a site, the distribution of displacements at that site does not simplify; the above method does not allow $p(2|13)$ to be expressed in terms of $p(2|1)$ or $p(2|3)$. This result is also true for continuous Markov processes in time: however, double-sided predictions with respect to past and future are usually not required.

4. The pinned chain

If a chain described by the energy functional (1.1) is pinned to the substrate at various points along its length, the same functional applies to each chain segment between adjacent pinning

sites, which provide boundary conditions for the segment. Let the chain be pinned at n positions $s_1 < s_2 < \cdots < s_n$ along its path, with fixed displacements $\phi_{P1}, \ldots, \phi_{Pn}$. For simplicity, the first derivative of displacement is not considered to be pinned, so each pinning site puts a smooth kink in the path of minimum energy. We seek to calculate the free energy of the pinned chain, also the distribution of chain displacement away from pinning sites. The internal energy is a quadratic function of the pinning displacements, equal to $4\kappa\xi^3\phi_P^2$ per pinning site if the sites are well separated. If the separation between two pinning sites is reduced below the persistence length $1/\xi$, the kinks are merged with a decrease or increase in energy according to whether the pinning displacements have the same or opposite signs.

Let $Z_{ab}^{(n)}(\Phi_a, \Phi_b)$ be the partition function for the chain with specified displacement vectors at the ends a, b and pinned as above at n sites. The composition law (equations (2.20) and (3.1)) suggests the recursion

$$Z_{ab}^{(n)}(\Phi_a, \Phi_b) = \frac{\xi}{C^2} \int \mathrm{d}\psi_n \, Z_{an}^{(n-1)}(\Phi_a, \Phi_n) Z_{nb}(\Phi_n, \Phi_b) \tag{4.1}$$

where $\phi_n = \phi_{Pn}$. When $n = 1$, the partition functions of the integrand describe unpinned chain segments and (3.1) is recovered on integrating out the pinning constraint. The dimensionless displacement vectors $\boldsymbol{u} = (\beta\kappa\xi^3)^{1/2}\Phi$ and equation (3.3) are used for explicit calculations. For any number of sites, the integral is of the form

$$\begin{aligned} J(u) &= \int \mathrm{d}v \exp(-\{\boldsymbol{u}\boldsymbol{H}\boldsymbol{u} + 2\boldsymbol{u}\cdot\boldsymbol{b}\}) \\ &= \left(\frac{\pi}{H_{22}}\right)^{1/2} \exp\left(-\left(H_{11} - \frac{H_{12}^2}{H_{22}}\right)u^2 - 2\left(b_1 - \frac{H_{12}}{H_{22}}b_2\right)u + \frac{b_2^2}{H_{22}}\right) \end{aligned} \tag{4.2}$$

where $\boldsymbol{u} = (u, v)$. The case $n = 1$ can be worked explicitly from (3.3), giving a multivariate Gaussian distribution in Φ_a, Φ_b biased by the pinning site. This form of distribution is maintained for any number of pinning sites, namely

$$\begin{aligned} Z_{ab}^{(n)}(\Phi_a, \Phi_b) &= \zeta_{ab}^{(n)} W(X_{ab}) \\ &\quad \times \exp\left(-[\boldsymbol{u}_a \boldsymbol{A}_{ab}^{(n)} \boldsymbol{u}_a + \boldsymbol{u}_a \boldsymbol{B}_{ab}^{(n)} \boldsymbol{u}_a + \boldsymbol{u}_b \boldsymbol{C}_{ab}^{(n)} \boldsymbol{u}_b + \boldsymbol{a}_{ab}^{(n)} \cdot \boldsymbol{u}_a + \boldsymbol{c}_{ab}^{(n)} \cdot \boldsymbol{u}_b]\right) \end{aligned} \tag{4.3}$$

where the matrices $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$ and vectors $\boldsymbol{a}$, $\boldsymbol{c}$ are functions of the reduced chain length X_{ab}, the number of sites and their reduced separations $x_{a1}, x_{12}, \ldots, x_{nb}$. The first factor is a fugacity and will be written as

$$\zeta_{ab}^{(n)} = w_{ab}^{(n)} \exp(-\Delta E_{ab}^{(n)}/k_B T) \tag{4.4}$$

where the pinning displacements appear only in $\Delta E_{ab}^{(n)}$. Recursive relations for these quantities are generated by substituting in (4.1). Only a closed subset of these formulae are exhibited, namely

$$\boldsymbol{C}_{ab}^{(n)} = \boldsymbol{A}^{\mathrm{S}}(x_{nb}) - \frac{\boldsymbol{B}^{\mathrm{S}}(x_{nb})\boldsymbol{P}_2\boldsymbol{B}(x_{nb})}{4H_{22}^{(n)}} \tag{4.5a}$$

$$\boldsymbol{c}_{ab}^{(n)} = \boldsymbol{B}^{\mathrm{S}}(x_{nb})\left(\boldsymbol{e}_1 - \frac{H_{12}^{(n)}}{H_{22}^{(n)}}\boldsymbol{e}_2\right)u_{Pn} - \frac{\boldsymbol{B}^{\mathrm{S}}(x_{nb})\boldsymbol{P}_2\boldsymbol{c}_{an}^{(n-1)}}{2H_{22}^{(n)}} \tag{4.5b}$$

$$w_{ab}^{(n)} = \left(\frac{\beta\kappa\xi^3}{\pi}\right)^{1/2} \left(\frac{|H(x_{an}, x_{nb})|}{H_{22}^{(n)}}\right)^{1/2} w_{an}^{(n-1)} \tag{4.5c}$$

$$\frac{\Delta E_{ab}^{(n)} - \Delta E_{an}^{(n-1)}}{k_B T} = \left(H_{11}^{(n)} - \frac{H_{12}^{(n)^2}}{H_{22}^{(n)}}\right)^2 u_{Pn}^2 + \left(c_1^{(n-1)} - \frac{H_{12}^{(n)}}{H_{22}^{(n)}}c_2^{(n-1)}\right)u_{Pn} - \frac{c_2^{(n-1)^2}}{4H_{22}^{(n)}} \tag{4.5d}$$

where

$$\boldsymbol{H}_{ab}^{(n)} \equiv \boldsymbol{C}_{an}^{(n-1)} + \boldsymbol{A}(x_{nb}). \tag{4.5e}$$

The regularization constant C does not appear, since the factor $1/C^2$ in (4.1) is removed on using (2.26). Starting formulae are $\boldsymbol{C}_{a1}^{(0)} = \boldsymbol{A}^{\mathrm{S}}(x_{a1})$, $\boldsymbol{c}_{a1}^{(0)} = 0$, $\zeta_{a1}^{(0)} = 1$, so $\boldsymbol{H}_{ab}^{(1)} \equiv \boldsymbol{H}(x_{a1}, x_{1b})$ as in (2.23). To save space, subscripts for the ends of the chain or chain segment are omitted when listing elements of matrices or vectors; thus $H_{ij}^{(n)} \equiv (\boldsymbol{H}_{ab}^{(n)})_{ij}$ refers to the whole chain but $c_i^{(n-1)} \equiv (\boldsymbol{c}_{an}^{(n-1)})_i$ according to (4.1). $\boldsymbol{e}_1 \equiv (1, 0)$ and $\boldsymbol{e}_2 \equiv (0, 1)$ are unit vectors and $\boldsymbol{P}_2 = \left(\begin{smallmatrix} 0 & 0 \\ 0 & 1 \end{smallmatrix}\right)$. As explained below, recursions for the remaining parameters are not required as they relate to the left-hand boundary a which is not replaced in (4.1).

It is now assumed that the chain is much longer than the persistence length and all pinning sites are similarly remote from the left-hand end ($X, x_{a1} \gg 1$). In this limit $\boldsymbol{A}_{ab}^{(n)} \approx \left(\begin{smallmatrix} 2 & 1 \\ 1 & 1 \end{smallmatrix}\right)$ and $\boldsymbol{B}_{ab}^{(n)}, \boldsymbol{a}_{ab}^{(n)} \approx 0$ for all n. The same assumption is required with respect to the right-hand end b, but cannot be imposed until the recursions (4.5) are exhausted. Then the matrix/vector coefficients in (4.3) revert to their values for the unpinned chain, and the change in the partition function produced by pinning is accounted for by the fugacity $\zeta_{ab}^{(n)}$. The corresponding change in free energy is

$$\Delta F_{ab}^{(n)} = \Delta E_{ab}^{(n)} - k_B T \ln w_{ab}^{(n)}. \tag{4.6}$$

The first term is a quadratic function of the pinning displacements, say

$$\Delta E_{ab}^{(n)} = 4\kappa\xi^3 \sum_{i=1}^{n} \sum_{j=i+1}^{n} \Gamma_{ij}^{(n)}(\boldsymbol{x}) \phi_{Pi} \phi_{Pj}. \tag{4.7}$$

where the dimensionless coefficients $\Gamma_{ij}^{(n)}$ are functions of the reduced site spacings $\boldsymbol{x} = (x_{12}, \ldots x_{n-1,n})$ between pinning sites, scaled so that $\Gamma_{ij}^{(n)} \approx \delta_{ij}$ when all separations are much greater than the persistence length ($x_{ij} \gg 1$). Recursions for these quantities can be extracted from (4.5d). All results apply only to sites in the interior of a long chain, which do not interact with end displacements.

By way of illustration, consider the lowest-order cases. For one pinning site, $\Delta E^{(1)} = 4\kappa\xi^3\phi_{P1}^2$ and $w^{(1)} = (4\kappa\xi^3/\pi k_B T)^{1/2}$. The changes in internal energy and entropy can be deduced thermodynamically; because $w^{(1)}$ is temperature-dependent the internal energy is equal to $\Delta E^{(1)} - k_B T/2$, which can be understood as a loss of one degree of freedom produced by pinning.

For two interior sites, the change in free energy depends on their reduced separation $x \equiv \xi(s_2 - s_1)$. Explicit formulae for this case are

$$4\Gamma_{11} = G_{11} - \frac{G_{12}^2}{G_{22}} - \frac{[B_{12} - (G_{12}/G_{22})B_{22}]^2}{4H_{22}^{(2)}} \tag{4.8a}$$

$$4\Gamma_{12} = \left(B_{11} + \frac{G_{12}}{G_{22}} B_{12}\right) - \frac{H_{12}^{(2)}}{H_{22}^{(2)}} \left(B_{12} - \frac{G_{12}}{G_{22}} B_{22}\right) \tag{4.8b}$$

$$4\Gamma_{22} = H_{11}^{(2)} - \frac{H_{12}^{(2)^2}}{H_{22}^{(2)}} \tag{4.8c}$$

where the dependence on x is suppressed and $\boldsymbol{G}(x) = \boldsymbol{H}(\infty, x)$ as before. Although the symmetry is not apparent in the formulae, $\Gamma_{11}(x) \equiv \Gamma_{22}(x)$ as expected. Figure 5 shows

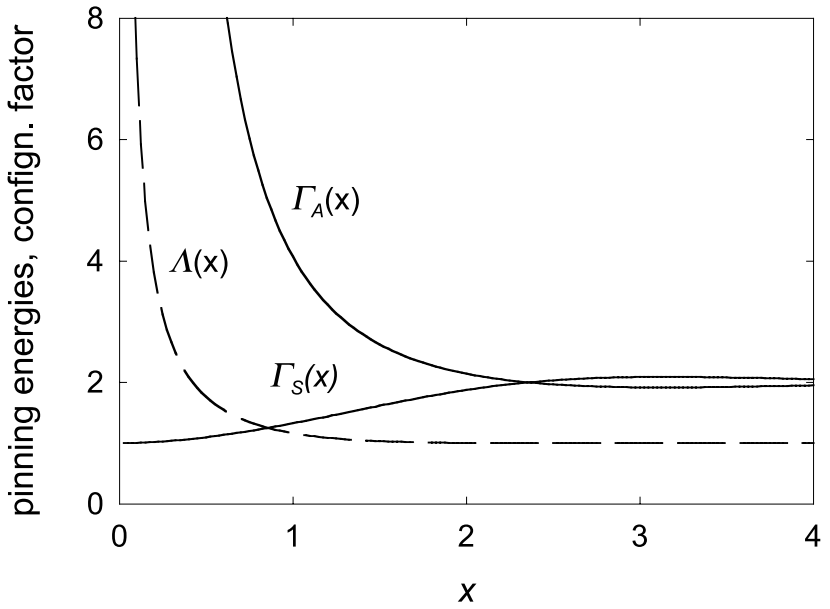

Figure 5. The energies $\Gamma_S(x) = 2\Gamma_{11}^{(2)} + \Gamma_{12}^{(2)}, \Gamma_A(x) = 2\Gamma_{11}^{(2)} - \Gamma_{12}^{(2)}$ of two pinning sites (equations (4.7) and (4.8), appendix C) as a function of their reduced separation x, for symmetric and antisymmetric pinning respectively (reduced displacements $u_{P1} = 1, u_{P2} = \pm 1$). At large separations ($x \gg 1$) the energy cost is twice that with one pinning site. When the two sites merge ($x \to 0$), they behave as one if the pinned displacements are equal, but there is a large energy cost (diverging as x^{-2}) for equal and opposite pinnings. The configuration factor $\Lambda(x) \equiv (\pi/4\beta\kappa\xi^3)w^{(2)}(x)$ tends to unity at large x and is independent of the pinning displacements.

the resulting 'two-kink' energy as a function of site spacing for symmetric ($\phi_{P2} = \phi_{P1}$) and antisymmetric ($\phi_{P2} = -\phi_{P1}$) sites, also a function $\Lambda(x)$ proportional to the common configuration factor $w^{(2)}$.

A related calculation can also describe how chain configurations are altered by pinning. Consider the distribution of displacements at a fixed position down the chain. Denote this position by c and the left- and right-hand ends by a and b as in figure 2. The composition law and the same recursion relations can be used to build the distribution $P^{(mn)}(\mathbf{\Phi}_c)$ of displacement vector $\mathbf{\Phi}_c = (\phi_c, \psi_c)$, with m pinning sites to the left and n to the right of point c. To build partition functions in the same way for the segments ac and cb, it is necessary to measure path distances from each end towards the middle and index the pinning sites in the same way, so that the sites nearest point c are indexed by m and n, respectively. Thus

$$P^{(mn)}(\mathbf{\Phi}_c) \propto Z_{ac}^{(m)}(\mathbf{\Phi}_a, \mathbf{\Phi}_c) Z_{bc}^{(n)}(\mathbf{\Phi}_b, \vec{\mathbf{\Phi}}_c) \tag{4.9}$$

where $\vec{\mathbf{\Phi}}_c = (\phi_c, -\psi_c)$. Again specializing to the interior of a long chain, we find that the reduced vector $\boldsymbol{u}_c$ is distributed as $\exp(-\{\boldsymbol{u}_c \boldsymbol{Q}^{(mn)} \boldsymbol{u}_c + \boldsymbol{q}^{(mn)} \cdot \boldsymbol{u}_c\})$, where

$$\boldsymbol{Q}^{(mn)} = \boldsymbol{C}_{ac}^{(m)} + \boldsymbol{C}_{bc}^{(n)^{\mathrm{S}}} \qquad \boldsymbol{q}^{(mn)} = \boldsymbol{c}_{ac}^{(m)} + \vec{\boldsymbol{c}}_{bc}^{(n)}. \tag{4.10}$$

It remains to integrate out the distribution over the second component of $\boldsymbol{u}_c$. Thus

$$p^{(mn)}(u) \propto \mathrm{e}^{-(Q_{11}^{(mn)} u^2 + q_1^{(mn)} u)} \int \mathrm{d}v \, \mathrm{e}^{-\{Q_{22}^{(mn)} v^2 + (2Q_{12}^{(mn)} u + q_2^{(mn)}) v\}} \tag{4.11}$$

which yields a shifted Gaussian distribution for the reduced displacement u at point c.

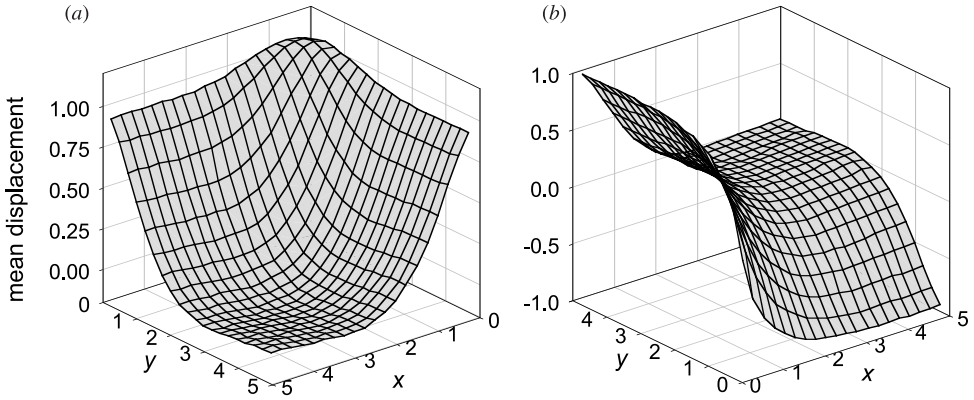

Figure 6. Mean chain displacement at a point between two pinning sites, separated by reduced distances x and y from the point in question, for (a) symmetric and (b) antisymmetric pinning as described in figure 5. When both pinning sites are remote ($x, y \gg 1$) the mean displacement tends to zero as in an unpinned chain. When one pinning site is near (x or $y \ll 1$), the mean displacement is close to the corresponding pinning value. When both sites are near, no conflict arises if the pinned displacements are equal (a), but when they are opposed (b), the mean value is very sensitive to small changes in their positions and $x = y = 0$ is a singular point of the function. To show this, the second figure has been rotated about a vertical axis.

The mean and variance of this distribution are, respectively,

$$\overline{u}^{(mn)} = -\frac{1}{2}\frac{q_1^{(mn)} - (Q_{12}^{(mn)}/Q_{22}^{(mn)})q_2^{(mn)}}{Q_{11}^{(mn)} - Q_{12}^{(mn)^2}/Q_{22}^{(mn)}} \qquad (4.12)$$

$$S^{(mn)^2} = \tfrac{1}{2}(Q_{11}^{(mn)} - Q_{12}^{(mn)^2}/Q_{22}^{(mn)})^{-1}.$$

All quantities are functions of the reduced distances x_{mc}, y_{nc} from c to the nearest pinning sites m and n to left and right, respectively, and the spacings between these and more distant sites.

These quantities are shown in figures 6 and 7 for the case $m = n = 1$ as a function of the reduced distances x and y to the pinning site on each side. The unbiased distribution found for the unpinned chain, with a standard deviation of $1/\sqrt{8}$, is found when $x, y \gg 1$. The distribution in the presence of just one site is revealed by removing the other site to a large distance. The mean displacement is controlled by the two pinning displacements, for example equal or opposite as shown in figure 6, whereas the variance is reduced close to a pinning site and its behaviour is independent of the pinning displacements.

5. Discussion

The problem of the harmonically confined worm-like chain is suggested by a form of the steric blocking model (Haselgrove 1973, Huxley 1973) for muscle regulation. Muscular contraction produced by binding of the motor-protein myosin to each thin filament (a double helix of actin) in striated muscle is regulated by the positions of a second filament (tropomyosin), which appears to span the thin filament. In this context, the worm-like chain is identified with the tropomyosin filament, which is though to roll on the surface of the actin filament to regulate myosin binding. A confining potential as a function of rolling angle will keep

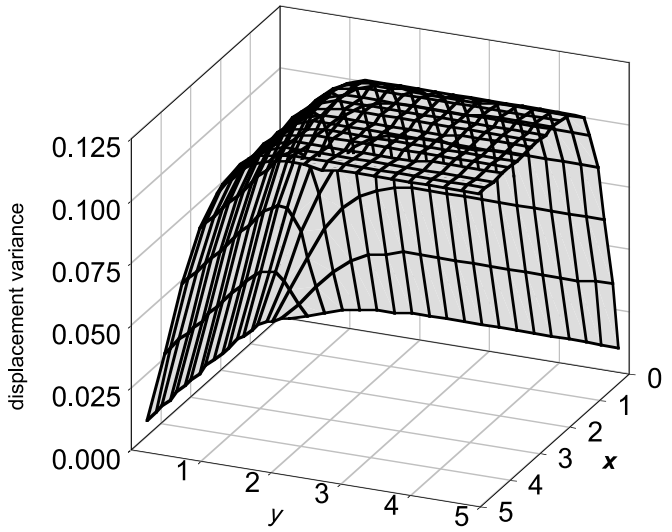

Figure 7. The displacement variance at a point between two pinning sites, as described in figure 6. This function is independent of the pinned displacements, and shrinks to zero (as x^2) when the point in question moves towards either pinning site.

this filament loosely aligned with the groove of the actin double-helix; related models have been proposed by Hill (1981). Although the topology of this surface is $\boldsymbol{S}^1 \times \boldsymbol{R}^1$ rather than $\boldsymbol{R}^2$, a harmonic potential can prevent the tropomyosin chain from rolling too far away from the groove, so its rolling angle $\phi(s)$ can be interpreted as the displacement of the present model.

The chain can be selectively pinned if molecules permanently attached to the chain can bind to bound to the surface of the thin filament. Through the molecule troponin, this mechanism is thought to be the basis of calcium-dependent muscle regulation (for example, Gagne *et al* 1995). Myosin molecules, which are never attached to the chain, can also impose localized constraints on chain configurations by binding to the thin filament, although the constraint is slightly less severe than pinning. The interplay between these two types of constraints is expected to form the basis of a cooperative theory of muscle regulation. This application of the model will be discussed elsewhere.

Alternative mathematical approaches to the solution of the path integral problem have already been mentioned. In particular, the composition relation (2.20) may be avoided if the eigenfunctions of (2.14) are known. In this respect the method of Davis and Southern (1997), which provides the inverse of (2.14), may be helpful.

Acknowledgments

I wish to thank Professor M Geeves (Biochemistry, Kent) and Professor R Streater (Mathematics, King's College) for helpful discussions, and the Wellcome Trust for a project grant. Symbolic-manipulation software (Waterloo Maple6^{TM}) was used to generate many of the algebraic results.

Appendix A. The coefficients c_k

The coefficients of the minimum path in (2.5) are obtained by fitting this function to the boundary displacements ϕ_a, ϕ_b and their derivatives, giving

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} & U_{13} & U_{14} \\ U_{21} & U_{22} & U_{23} & U_{24} \\ -U_{21} & 1-U_{21} & -U_{23} & -U_{24} \\ 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \phi_a \\ \psi_a \\ \phi_b \\ \psi_b \end{pmatrix} \tag{A.1}$$

where

$$\begin{aligned} U_{11} &= \frac{\cos^2 X - \cosh^2 X}{d(X)} & U_{21} &= \frac{\sinh X \cosh X + \sin X \cos X}{d(X)} \\ U_{12} &= \frac{\sin X \cos X - \sinh X \cosh X}{d(X)} & U_{22} &= \frac{\sinh^2 X}{d(X)} \\ U_{13} &= \frac{2 \sinh X \sin X}{d(X)} & U_{23} &= \frac{\sinh X \cos X + \cosh X \sin X}{d(X)} \\ U_{14} &= \frac{\sinh X \cos X - \cosh X \sin X}{d(X)} & U_{24} &= \frac{\sinh X \sin X}{d(X)} \end{aligned} \tag{A.2}$$

and $d(X) = \sinh^2 X - \sin^2 X$ as before. These results are required to obtain (2.10).

Appendix B. The determinant of (2.14) with $\lambda = 0$

For $\lambda = 0$, the matrix (2.14) is closely related to the square of the matrix for an energy term involving the first path derivative, as

$$\begin{pmatrix} 2 & -1 & & & & 0 \\ -1 & 2 & -1 & & & \\ & \cdot & \cdot & \cdot & & \\ & & \cdot & \cdot & \cdot & \\ & & & -1 & 2 & -1 \\ 0 & & & & -1 & 2 \end{pmatrix}^2 = \begin{pmatrix} 5 & -4 & 1 & & & 0 \\ -4 & 6 & -4 & 1 & & \\ 1 & -4 & 6 & -4 & 1 & \\ & 1 & -4 & 6 & -4 & 1 \\ & & 1 & -4 & 6 & -4 \\ 0 & & & 1 & -4 & 5 \end{pmatrix} \tag{B.1}$$

differs from (2.14) only in the first and last diagonal entries. The determinant is $(N+1)^2$ (Kleinert 1995) if the matrix is $N \times N$. Let D_N be the determinant of (2.14) and E_N the determinant of this matrix with either the first or last diagonal entry equal to 6. Two Laplace expansions (Aitken 1956), starting with that of D_N about (B1), gives

$$\begin{aligned} D_N &= (N+1)^2 + 2E_{N-1} + D_{N-2} \\ E_{N-1} &= N^2 + E_{N-2}. \end{aligned} \tag{B.2}$$

Hence $E_{N-1} = N(N+1)(2N+1)/6$ and $D_N - D_{N-2} = (N+1)(2N^2+4N+3)/3$, with starting values $D_1 = 6$, $D_2 = 20$. Hence

$$D_N \approx N^4/12 + \mathrm{O}(N)^3. \tag{B.3}$$

Thus changing the boundary diagonals from 5 to 6 changes the determinant profoundly, from $\mathrm{O}(N^2)$ to $\mathrm{O}(N^4)$. This adjustment arises from the need to specify displacement derivatives at each end, without which the finite-difference terms in (2.13) could be restricted to the range $n = (1, N-1)$.

Appendix C. Formulae for two-site pinning energies

The coefficients in (2.17) generate the functions $\Gamma_S(x) = 2\Gamma_{11}^{(2)}(x) + \Gamma_{12}^{(2)}(x)$ and $\Gamma_A(x) = 2\Gamma_{11}^{(2)}(x) - \Gamma_{12}^{(2)}(x)$ for the energy of the chain pinned at two sites at reduced separation x, with either symmetric or antisymmetric pinning ($u_{P2}/u_{P1} = 1, -1$, respectively). Explicit forms for these functions are $N_S(x)/D(x)$, $N_A(x)/D(x)$, where

$$\begin{aligned}N_S(x) = 4(&-3\sinh x \sin x + 2\cosh 2x - \cosh 4x + \sin x \cosh 3x + \cos x \cosh 3x + 2\sinh 2x\\ &- \sinh 4x + \cos x \sinh 3x - \cosh 2x \cos 2x + \sin x \sinh 3x + \cosh 2x \sin 2x\\ &+ \cosh x \cos 3x + \sinh x \cos 3x - 2\sinh x \cos x - 3\cosh x \sin x\\ &- \cos 2x \sinh 2x + \sin 2x \sinh 2x - 2\cosh x \cos x)\end{aligned}$$

$$\begin{aligned}N_A(x) = 4(&3\sinh x \sin x + 2\cosh 2x - \cosh 4x - \sin x \cosh 3x - \cos x \cosh 3x + 2\sinh 2x\\ &- \sinh 4x - \cos x \sinh 3x - \cosh 2x \cos 2x - \sin x \sinh 3x + \cosh 2x \sin 2x\\ &- \cosh x \cos 3x - \sinh x \cos 3x + 2\sinh x \cos x + 3\cosh x \sin x\\ &- \cos 2x \sinh 2x + \sin 2x \sinh 2x + 2\cosh x \cos x)\end{aligned}$$

$$\begin{aligned}D(x) = &-2\cosh 4x + 6\cosh 2x - 5 - 2\sinh 4x + 6\sinh 2x - 2\cosh 2x \cos 2x + 2\cos 2x\\ &+4\cosh 2x \sin 2x - 6\sin 2x - 2\cos 2x \sinh 2x + 4\sin 2x \sinh 2x\\ &+\cos 4x + \sin 4x.\end{aligned}$$

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