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Variational methods for constrained polymer dynamics

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Abstract. The dynamics of an idealized polymer chain (bead-spring model) is treated as a special case of Brownian motion in a potential. In free space the corresponding Langevin description is sufficient. In the presence of constraints on the dynamics one has to apply the full Fokker–Planck formalism. In general, the ensuing boundary value problem is not analytically solvable, so we resort to approximation methods. For diffusive motion in a potential there exists a natural Hilbert space on which the Fokker–Planck operator is positive (semi-)definite. Consequently, the problem is amenable to variational methods. Here, we investigate exemplarily the relaxation of a Rouse chain fixed with one end to a planar, impenetrable surface and obtain the relaxation spectrum approximately using the Rayleigh–Ritz scheme. This may be the first instance in which this formalism is applied to polymer dynamics.

1. Introduction

The dynamical behaviour of macromolecules is of fundamental interest for many technical applications of polymer materials. A basic concept for the understanding of the diffusive motion of long flexible chain molecules is the Rouse model [1, 2]. In this model a polymer is idealized as a chain of Brownian particles connected by harmonic springs. The model provides a reasonable picture for dense polymer melts, if the chain length N does not exceed the so-called entanglement threshold [2, 3], as also shown by recent computer simulations [4, 5].

Polymers in confined geometries can also be modelled through the Rouse model. The simplest case is perhaps that of a chain fixed to a solid, impenetrable wall. Other important examples are polymers squeezed between two walls or confined in a tube [6] or in a pore [7]. A common property of all these situations is that the corresponding Rouse models are not amenable to a purely analytical treatment, since the modes of the original linear equation become coupled. In some situations, such as polymers in thin tubes [8] or in porous media [7] characteristic properties of the constrained dynamics can be obtained using *ad hoc* models (reptation, entropic trapping), but a unified theoretical treatment is still missing.

Here we use the Rayleigh–Ritz variational scheme (which is well known in quantum mechanics, see also a recent application to nonlinear dynamics [9]) to evaluate the relaxation modes of a Rouse chain under constraints. The procedure starts from a description of the chain's dynamics by means of the associated Fokker–Planck equation (in polymer literature it is often called the Smoluchowski equation). Due to the fact that for Brownian motion in a potential detailed balance holds, the Fokker–Planck operator is positive (semi-)definite on the appropriate Hilbert space, so that (Rayleigh–Ritz) variational techniques can be used. This variational approach is a viable alternative to computer simulations to obtain numerical results for constrained polymer dynamics. In this paper we apply this formalism to the case

of a chain fixed with one end to a planar solid wall, including numerical calculations of the relaxation spectrum. Applications of the Rayleigh–Ritz scheme to other physical situations such as polymers confined in a narrow gap between two plates will be the topic of an ensuing publication. In general, the variational approach propagated here—due to its analytical roots—can be a short-cut, when compared with direct computer simulations, to numerical evaluations for specific situations.

The paper is organized as follows. In section 2 we present a brief discussion of the general formalism for Brownian dynamics in a potential. This provides the background for treating the dynamics of a tethered polymer by means of the Fokker–Planck equation. The whole chain consisting of N beads corresponds to a point in the $3N$ -dimensional configuration space. The potential for this ‘point particle’ stems from the Hookean springs which connect the beads. We then reformulate the Fokker–Planck equation as an eigenvalue problem, and solve it numerically through Rayleigh–Ritz methods.

In section 3 the general formalism is applied to the dynamics of a tethered polymer chain. A separation of variables allows us to treat the different spatial directions independently. For the motion parallel to the surface the traditional Langevin approach and the Fokker–Planck ansatz are equivalent. For the motion perpendicular to the surface the constraints are incorporated as boundary conditions for the Fokker–Planck equation. The Rayleigh–Ritz method introduced in section 2 is now used to determine the relaxation spectrum. The corresponding matrix elements are calculated by means of recursion relations, based on truncated Gaussian integrals. A derivation of these integrals has been kindly provided to us by Glasser [15], and is presented in the appendix. Finally, we discuss our numerical results in section 4 and show how their qualitative features can be understood using a mean-field model.

Throughout the paper we use the following notation:

- capital indices $K, L = 1, \dots, N$ enumerate the beads of the Rouse chain.
- Lower case indices $i, j = 1, \dots, \infty$ label sets of functions in the appropriate Hilbert space.
- Arbitrary functions in Hilbert space are designated by ψ_i, χ_i , while the φ_i denote eigenfunctions of the Fokker–Planck operator.

2. Brownian dynamics in a potential

2.1. The Fokker–Planck approach

Standard models for the dynamics of polymers start from the damped (diffusive) motion of chain segments. In the Rouse model [1, 2], the segments are idealized as beads which are connected by Hookean springs. For a chain consisting of N beads, the collection of all their positions corresponds to a point in a $3N$ -dimensional position space, and the collective motion of the chain may be described as the diffusion of this $3N$ -dimensional point under the influence of the spring forces. Without external constraints, the related stochastic process corresponds to a $3N$ -dimensional Ornstein–Uhlenbeck process [10].

In order to set the scene for general constrained dynamics, we start by discussing the Brownian motion of a point particle under the influence of a deterministic force field $\mathbf{F}(\mathbf{r})$. The time evolution of the particle’s probability distribution $p(\mathbf{r}, t)$ is governed by the Fokker–Planck equation [11]

$$\frac{\partial}{\partial t} p(\mathbf{r}, t) = [\Delta - \nabla \cdot \mathbf{F}(\mathbf{r})] p(\mathbf{r}, t) \quad (1)$$

which is a superposition of a diffusive and a deterministic (Liouville-type) term. If the

diffusion is restricted to a domain Ω , one also has to take into account what happens at the boundary $\partial\Omega$. Here we focus on the case where the particle is reflected elastically at the boundary. This amounts to the condition

$$\mathbf{n} \cdot \mathbf{J}(\mathbf{r}, t) = 0 \quad \text{on } \partial\Omega \quad (2)$$

with the probability current given by

$$\mathbf{J}(\mathbf{r}, t) = [-\nabla + \mathbf{F}(\mathbf{r})]p(\mathbf{r}, t). \quad (3)$$

A special situation occurs when the force field is conservative, and hence is related to some potential $U(\mathbf{r})$:

$$\mathbf{F}(\mathbf{r}) = -\nabla U(\mathbf{r}). \quad (4)$$

In this case the equilibrium solution to equation (1) is immediate:

$$p_0(\mathbf{r}) = \frac{1}{Z} e^{-U(\mathbf{r})} \quad (5)$$

where Z is the normalization constant. The factorization

$$p(\mathbf{r}, t) = q(\mathbf{r}, t) \cdot p_0(\mathbf{r}) \quad (6)$$

transforms equation (1) into a more convenient form, namely

$$\frac{\partial}{\partial t} q(\mathbf{r}, t) = [\Delta + \mathbf{F}(\mathbf{r}) \cdot \nabla]q(\mathbf{r}, t) = -\mathcal{L}q(\mathbf{r}, t) \quad (7)$$

which is formally the adjoint of equation (1). Here we have introduced the diffusion operator

$$\mathcal{L} = -\Delta - \mathbf{F} \cdot \nabla \quad (8)$$

with the minus sign chosen such that the spectrum of \mathcal{L} consists of nonnegative eigenvalues (see below). Note that \mathcal{L} can also be written as

$$\mathcal{L} = -e^{U(\mathbf{r})} \nabla e^{-U(\mathbf{r})} \nabla. \quad (9)$$

Instead of the mixed boundary conditions for $p(\mathbf{r}, t)$, equation (2), the boundary conditions for $q(\mathbf{r}, t)$ are simply of Neumann type:

$$\mathbf{n} \cdot \nabla q(\mathbf{r}, t)|_{\partial\Omega} = 0. \quad (10)$$

The solution of equation (7) for any given initial condition $q(\mathbf{r}, t = 0) = q_0(\mathbf{r})$ can be formally written as

$$q(\mathbf{r}, t) = e^{-t\mathcal{L}} q_0(\mathbf{r}) \quad (11)$$

or, by means of the associated integral kernel, as

$$q(\mathbf{r}, t) = \int p(\mathbf{r}, 0 \rightarrow \mathbf{r}', t) q_0(\mathbf{r}') d\mathbf{r}' \quad (12)$$

with $p(\mathbf{r}, 0 \rightarrow \mathbf{r}', t)$ denoting the transition probability for the diffusion process subject to the appropriate boundary conditions.

2.2. Rayleigh–Ritz approximation

The main step towards a solution of equation (7) is an eigenfunction expansion with respect to the spatial component. Given a complete set $\varphi_i(\mathbf{r})$ of (normalized) eigenfunctions for \mathcal{L} , i.e.

$$\mathcal{L}\varphi_i(\mathbf{r}) = \omega_i\varphi_i(\mathbf{r}) \quad (13)$$

where the φ_i obey equation (10), the transition probability can be written as

$$p(\mathbf{r}, 0 \rightarrow \mathbf{r}', t) = \sum_i \varphi_i(\mathbf{r})\varphi_i(\mathbf{r}')p_0(\mathbf{r}')e^{-\omega_i t}. \quad (14)$$

If no boundary conditions have to be accounted for, the eigenvalue problem equation (13) can be transformed into an equivalent Schrödinger problem with

$$\mathcal{L}_{\text{Schröd}} = -\Delta + V(\mathbf{r}) \quad (15)$$

where the Schrödinger potential $V(\mathbf{r})$ is related to the original potential $U(\mathbf{r})$ by

$$V(\mathbf{r}) = \frac{1}{4}(\nabla U(\mathbf{r}))^2 - \frac{1}{2}\Delta U(\mathbf{r}). \quad (16)$$

In general, however, such a transformation is not practical in the presence of boundary conditions. For instance, the simple Neumann boundary conditions equation (10) are transformed to position-dependent mixed boundary conditions of the form

$$[\mathbf{n} \cdot \nabla + \frac{1}{2}(\mathbf{n} \cdot \nabla U(\mathbf{r}))]\varphi(\mathbf{r}) = 0. \quad (17)$$

Another approach to the solution of the eigenvalue problem equation (13) for the Fokker–Planck equation (7), inspired by quantum mechanical techniques, uses variational methods. Generally, such methods may be applied to arbitrary positive definite, self-adjoint operators on some Hilbert space. For diffusion problems satisfying the detailed balance condition with respect to some equilibrium distribution $p_0(\mathbf{r})$, a suitable Hilbert space, rendering the diffusion operator positive definite, is naturally provided by $L^2(\Omega, p_0 d\mathbf{r})$. The corresponding weighted scalar product is defined by means of the equilibrium distribution $p_0(\mathbf{r})$ of equation (5)

$$\langle \chi, \psi \rangle_{p_0} = \int_{\Omega} \chi^*(\mathbf{r})\psi(\mathbf{r})p_0(\mathbf{r}) d\mathbf{r} \quad (18)$$

(with the asterisk denoting complex conjugation). The unbounded diffusion operator \mathcal{L} as given in equation (9) is symmetric with respect to the scalar product $\langle \cdot, \cdot \rangle_{p_0}$. Apart from the zero eigenvalue corresponding to the equilibrium state, \mathcal{L} is even positive definite: For any functions $\chi(\mathbf{r})$ and $\psi(\mathbf{r})$ belonging to the domain of \mathcal{L} subject to Neumann boundary conditions we have

$$\begin{aligned} \langle \chi, \mathcal{L}\psi \rangle_{p_0} &= -\frac{1}{Z} \int_{\Omega} \chi^*(\mathbf{r})(e^{U(\mathbf{r})}\nabla e^{-U(\mathbf{r})}\nabla\psi(\mathbf{r}))e^{-U(\mathbf{r})} d\mathbf{r} \\ &= \frac{1}{Z} \int_{\Omega} (\nabla\chi^*(\mathbf{r}))(\nabla\psi(\mathbf{r}))e^{-U(\mathbf{r})} d\mathbf{r} - \frac{1}{Z} \int_{\partial\Omega} \chi^*(\mathbf{r})(\mathbf{n} \cdot \nabla\psi(\mathbf{r}))e^{-U(\mathbf{r})} d\sigma \\ &= \langle \nabla\chi, \nabla\psi \rangle_{p_0}. \end{aligned} \quad (19)$$

Here, $\partial\Omega$ denotes the boundary of the domain Ω , and the integral over $\partial\Omega$ vanishes due to the Neumann boundary conditions. The eigenvalue problem equation (13) is now equivalent to

$$\langle \nabla\psi, \nabla\varphi_i \rangle_{p_0} = \omega_i \langle \psi, \varphi_i \rangle_{p_0} \quad \text{for any } \psi \quad (20)$$

provided the $\varphi_i(\mathbf{r})$ obey Neumann boundary conditions. Due to the growth properties of $p_0(\mathbf{r})$ at infinity, \mathcal{L} usually has, as in the case of Schrödinger equations, a discrete spectrum.

In the concrete case discussed below the relevant domain Ω for the differential equation is unbounded. Instead of applying some kind of finite element methods it seems more appropriate to use the Rayleigh–Ritz scheme for a numerical solution of the variational problem, equation (20).

The choice of some basis $\psi_i(\mathbf{r})$ of globally defined functions in $L^2(\Omega, p_0 d\mathbf{r})$ formally transforms equation (20) into an infinite-dimensional algebraic eigenvalue problem. To simplify the calculations we do not require that the ψ_i 's be orthogonal to each other. Hence, we are led to a generalized eigenvalue problem of the form

$$\mathbb{L}\mathbf{v}_i = \omega_i \mathbb{S}\mathbf{v}_i. \quad (21)$$

In order to avoid taking care of the zero eigenvalue corresponding to the one-dimensional subspace of constant functions, we restrict (21) to the orthogonal complement \mathcal{H} of that subspace. Implementing this projection, the matrix elements of \mathbb{L} and \mathbb{S} are then given by

$$\mathbb{L}_{ij} = \langle \psi_i, \mathcal{L}\psi_j \rangle_{p_0} = \langle \nabla\psi_i, \nabla\psi_j \rangle_{p_0} \quad (22)$$

and

$$\mathbb{S}_{ij} = \langle \psi_i, \psi_j \rangle_{p_0} - \langle \psi_i \rangle_{p_0} \langle \psi_j \rangle_{p_0}. \quad (23)$$

The vectors \mathbf{v}_i are determined by the relation $\varphi_i(\mathbf{r}) = \sum (\mathbf{v}_i)_j \psi_j(\mathbf{r})$.

In the Rayleigh–Ritz approximation scheme, we restrict equation (21) to the sequence $\mathcal{H}^{(n)}$ of finite-dimensional subspaces spanned by the first n basis elements ψ_1, \dots, ψ_n . For fixed i the approximate eigenvalues $\omega_i^{(n)}$, $n = i, \dots$ form a decreasing sequence which bound the true eigenvalue ω_i from above, see [12].

3. The Fokker–Planck approach to constrained Rouse dynamics

The dynamics of polymer chains in semidilute melts is usually described in terms of the Langevin equation (Rouse model) [2]

$$\zeta \dot{\mathbf{R}}_K = \kappa(\mathbf{R}_{K+1} - 2\mathbf{R}_K + \mathbf{R}_{K-1}) + \boldsymbol{\xi}_K \quad (24)$$

where the position of the K th bead is denoted by \mathbf{R}_K , and $\boldsymbol{\xi}_K$ are Gaussian random forces related to the temperature T through

$$\langle \boldsymbol{\xi}_K(s) \boldsymbol{\xi}_L(t) \rangle = 2\zeta k_B T \delta_{KL} \delta(s - t). \quad (25)$$

In order to incorporate geometric restrictions on the chain's motion, however, we start with the Fokker–Planck equation associated with equation (24). The ‘point-particle’ of section 2 now corresponds to the whole chain of N beads, described as a point $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ in the $3N$ -dimensional configuration space, where $\mathbf{r}_K = (x_K, y_K, z_K)$ denotes the (dimensionless) position vector of the K th monomer. In the absence of an additional external field, $U(\mathbf{r})$ is taken as the harmonic potential of the Hookean springs, representing the chain connectivity. In the following we will consider the case of a chain fixed with one end at the origin $\mathbf{r}_0 = 0$ (see figure 1). The potential is then given by

$$\begin{aligned} U(\mathbf{r}_1, \dots, \mathbf{r}_N) &= \frac{1}{2} [\mathbf{r}_1^2 + (\mathbf{r}_1 - \mathbf{r}_2)^2 + \dots + (\mathbf{r}_{N-1} - \mathbf{r}_N)^2] \\ &= \frac{1}{2} \sum_{K,L=1}^N \mathbb{M}_{KL} \mathbf{r}_K \mathbf{r}_L \end{aligned} \quad (26)$$

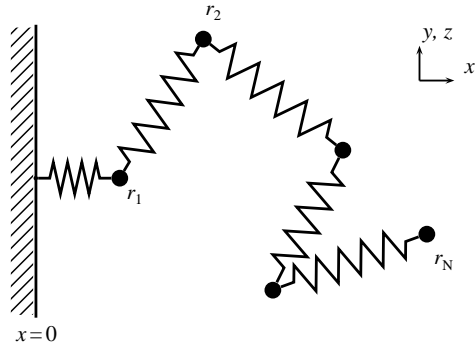


Figure 1. A Rouse chain fixed at a planar surface.

where we have introduced the so-called Rouse matrix \mathbb{M} , which has the form

$$\mathbb{M} = \begin{pmatrix} 2 & -1 & & & 0 \\ -1 & 2 & \ddots & & \\ & \ddots & \ddots & \ddots & \\ & & \ddots & 2 & -1 \\ 0 & & & -1 & 1 \end{pmatrix}. \quad (27)$$

Inserting this harmonic potential into equation (7) we obtain the Fokker–Planck equation for the Rouse chain:

$$\frac{\partial}{\partial t} q(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \sum_K [\Delta_{\mathbf{r}_K} - \sum_L \mathbb{M}_{KL} \mathbf{r}_L \cdot \nabla_{\mathbf{r}_K}] q(\mathbf{r}_1, \dots, \mathbf{r}_N, t). \quad (28)$$

If the motion of the monomers is restricted to some region \mathcal{R} of the three-dimensional position space, the relevant domain for equation (28) is $\Omega = \mathcal{R}^N$, and this equation has to be supplemented with the corresponding Neumann boundary conditions, equation (10).

3.1. A Rouse chain tethered to an impenetrable surface

As a concrete example for geometric restrictions we will now consider a Rouse chain fixed (tethered) with one of its ends to an impenetrable planar surface. Our main interest is concerned with its relaxation spectrum. Additionally, inspired by experiments with certain dielectrically active tethered polymer chains, we will furthermore investigate the autocorrelation function of the chain's end-to-end vector. In a linear approximation, this function determines the dielectric response of the samples to an alternating, homogeneous electric field (cf [13]).

The surface will be taken here to be the yz -plane at $x = 0$. The chain is supposed to be fixed at the origin $\mathbf{r}_0 = 0$ (see figure 1).

Due to the linearity of the Hookean forces, the corresponding stationary eigenvalue problem can be separated into three independent components, each space direction leading to an N -dimensional equation (N being the number of beads)

$$[-\Delta_{\zeta} + \mathbb{M}\zeta \cdot \nabla_{\zeta}] \varphi_i(\zeta) = \omega_i^{(\zeta)} \varphi_i(\zeta). \quad (29)$$

In equation (29) ζ now stands for any direction x , y or z , and $\zeta = (\zeta_1, \dots, \zeta_N)$. Since the force components $F_K = -\sum_L \mathbb{M}_{KL} \zeta_L$ depend on ζ_{K-1} and ζ_{K+1} , a further separation of variables will only be possible in the absence of boundary conditions.

3.1.1. Direction parallel to the surface. Parallel to the surface, equation (29) has to be solved on the whole \mathbb{R}^N without any specific boundary conditions, apart from the usual integrability requirements. This is a standard exercise and furnishes the same results as the classical treatment of Rouse dynamics by Langevin methods. We summarize the main points which we also need later for a comparison with the motion perpendicular to the surface, see [13] for details.

By a transformation to normal coordinates $(u_K)_{K=1,\dots,N}$ —defined in terms of the orthogonal eigenvectors of the Rouse matrix \mathbb{M} —the N -dimensional Fokker–Planck equation separates into N single ordinary differential equations of Hermite type. Hence, the solutions of the eigenvalue problem are suitable products of (scaled) Hermite polynomials [14]

$$\varphi_i(u_1, \dots, u_N) = \text{constant } H_{i_1} \left(u_1 \sqrt{\omega_1^R/2} \right) \dots H_{i_N} \left(u_N \sqrt{\omega_N^R/2} \right). \quad (30)$$

The corresponding eigenvalues of the form

$$\omega_{(i_1, \dots, i_N)} = i_1 \omega_1^R + \dots + i_N \omega_N^R \quad (31)$$

are linear combinations with nonnegative integer coefficients of the eigenvalues ω_K^R of \mathbb{M}

$$\omega_K^R = 4 \sin^2 \left[\left(\frac{2K-1}{2N+1} \right) \frac{\pi}{2} \right] \quad K = 1, \dots, N. \quad (32)$$

The ω_K^R are the *fundamental* Rouse frequencies.

Provided that with these data one can immediately calculate the correlation matrix $\mathbb{C}^{(q)}(t)$, which is completely determined by the Rouse matrix

$$\mathbb{C}^{(q)}(t) = \langle (\zeta(0) - \bar{\zeta}) \otimes (\zeta(t) - \bar{\zeta}) \rangle = \mathbb{M}^{-1} e^{-t\mathbb{M}} \quad (33)$$

i.e. the fluctuations of the positions for the K th and L th bead (in $\zeta = y$ - or z -direction) are correlated according to

$$\langle (\zeta_K(0) - \bar{\zeta}_K)(\zeta_L(t) - \bar{\zeta}_L) \rangle = (\mathbb{M}^{-1} e^{-t\mathbb{M}})_{KL}. \quad (34)$$

In particular it turns out that only the fundamental Rouse frequencies contribute to linear relaxation phenomena. As will be shown below, the situation changes drastically in the presence of boundary conditions, where anharmonicities influence the relaxation spectrum.

3.1.2. Direction perpendicular to the surface. For the x -direction normal to the surface the relevant domain is the region

$$\Omega = \{ \mathbf{x} | x_K \geq 0, K = 1, \dots, N \} \quad (35)$$

with $\mathbf{x} = (x_1, \dots, x_N)$. The Neumann boundary conditions (10) for the corresponding eigenfunctions $\varphi_i(\mathbf{x})$ are:

$$\frac{\partial}{\partial x_K} \varphi_i(\mathbf{x}) = 0 \quad \text{at } x_K = 0. \quad (36)$$

In contrast to the case without boundary conditions discussed in section 3.1.1, we cannot solve this boundary value problem in closed, analytical form (except for the simple case $N = 1$). Due to the reflections at the surface the individual Rouse modes are coupled, and the problem no longer separates. A transformation to the normal coordinates of the Rouse matrix \mathbb{M} leads to nondiagonal boundary conditions. However, an auxiliary, approximate model (with modified boundary conditions), based on the separation method in the parallel case, can at least be introduced to obtain lower bounds for the spectral values, see [13] for details.

In the following section we will apply the Rayleigh–Ritz approximation scheme to investigate the Rouse dynamics perpendicular to the interface. Concentrating on the dynamics of the chain end, a simple physical model for the resulting (approximate) spectrum will be given in terms of a mean-field approximation in the concluding section.

3.2. Computational steps for the Rayleigh–Ritz approximation

3.2.1. Choice of basis functions. The main criteria for a suitable choice of basis functions for the Rayleigh–Ritz approximation are:

- the Neumann boundary conditions have to be satisfied;
- the matrix elements \mathbb{L}_{ij} and \mathbb{S}_{ij} , determined by N -dimensional integrals over the region of equation (35), must be evaluated with sufficient accuracy.

Due to the first requirement, the Hermite polynomials, equation (30), have to be ruled out as candidates, since they do not obey the correct boundary conditions.

Instead, a convenient set of basis functions for our domain Ω consists of polynomials of the form

$$\psi_{(i_1, \dots, i_N)}(\mathbf{x}) = c x_1^{i_1} \dots x_N^{i_N} \quad \text{with } i_K \neq 1 \quad \sum i_K > 0. \quad (37)$$

The condition $i_K \neq 1$ guarantees that the $\psi_{(i_1, \dots, i_N)}$ obey the Neumann boundary conditions $\partial/\partial x_K[\psi_{(i_1, \dots, i_N)}] = 0$ at $x_K = 0$.

In order to keep the corresponding matrix elements of a reasonable size, the freely adjustable prefactors c in (37) are taken as

$$c(i_1, \dots, i_N) = (i_1! \dots i_N!)^{-1}. \quad (38)$$

Having chosen this set of basis functions indexed by some multi-index, i.e. by an N -tuple (i_1, \dots, i_N) of nonnegative integers, the next step consists of arranging them in consecutive order, and we denote by i the integer corresponding to the multi-index (i_1, \dots, i_N) .

3.2.2. Matrix elements. When inserting the above-chosen polynomials into equations (22) and (23) we have to compute various moments with respect to the equilibrium distribution. The normalization constants are

$$Z_N^U = \int_{\Omega} e^{-U_N(x_1, \dots, x_N)} d^N x \quad (39)$$

with $U_N(\mathbf{x})$ being the part of the harmonic potential corresponding to the x -components of the monomer positions

$$\begin{aligned} U_N(x_1, \dots, x_N) &= \frac{1}{2}(x_1^2 + (x_1 - x_2)^2 + \dots + (x_{N-1} - x_N)^2) \\ &= \frac{1}{2} \mathbf{x} \cdot \mathbb{M} \mathbf{x}. \end{aligned} \quad (40)$$

Additionally we need the auxiliary normalization constants

$$Z_N^V = \int_{\Omega} e^{-V_N(x_1, \dots, x_N)} d^N x \quad (41)$$

with

$$\begin{aligned} V_N(x_1, \dots, x_N) &= \frac{1}{2}(x_1^2 + (x_1 - x_2)^2 + \dots + (x_{N-1} - x_N)^2 + x_N^2) \\ &= \frac{1}{2} \mathbf{x} \cdot \mathbb{N} \mathbf{x} \end{aligned} \quad (42)$$

where

$$\mathbb{N} = \begin{pmatrix} 2 & -1 & & & 0 \\ -1 & 2 & \ddots & & \\ & \ddots & \ddots & \ddots & \\ & & \ddots & 2 & -1 \\ 0 & & & -1 & 2 \end{pmatrix} \quad (43)$$

corresponding to a polymer loop fixed at the surface. The analytical determination of Z_N^U and Z_N^V was communicated to us by Glasser [15] and is presented in the appendix. The results are (see also [16]):

$$Z_N^U = \left(\frac{\pi}{2}\right)^{N/2} \frac{(2N-1)!!}{N!} \quad (44)$$

and

$$Z_N^V = (2\pi)^{N/2} (N+1)^{-3/2}. \quad (45)$$

Furthermore, for $i_k \geq 0$ we have to calculate the moments

$$u_N(i_1, \dots, i_N) := \int_{\Omega} x_1^{i_1} \dots x_N^{i_N} e^{-U(x_1, \dots, x_N)} d^N x \quad (46)$$

as well as

$$v_N(i_1, \dots, i_N) := \int_{\Omega} x_1^{i_1} \dots x_N^{i_N} e^{-V(x_1, \dots, x_N)} d^N x. \quad (47)$$

As we proceed to show, the moments can be determined using suitable recursion relations. Note first that both \mathbb{M}^{-1} and \mathbb{N}^{-1} exist and are given by

$$\mathbb{M}^{-1} = \begin{pmatrix} 1 & \dots & \dots & 1 \\ \vdots & 2 & \dots & 2 \\ \vdots & \vdots & \ddots & \\ \vdots & \vdots & & \\ 1 & 2 & & N \end{pmatrix} \quad (48)$$

and

$$\mathbb{N}^{-1} = \frac{1}{N+1} \begin{pmatrix} N & N-1 & \dots & 2 & 1 \\ N-1 & 2(N-1) & \dots & 4 & 2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 2 & 4 & \dots & 2(N-1) & N-1 \\ 1 & 2 & \dots & N-1 & N \end{pmatrix}. \quad (49)$$

Thus we can write

$$\mathbf{x} \cdot \mathbf{e}^{-U_N(\mathbf{x})} = -\mathbb{M}^{-1} \cdot \nabla \mathbf{e}^{-U_N(\mathbf{x})} \quad (50)$$

and likewise

$$\mathbf{x} \cdot \mathbf{e}^{-V_N(\mathbf{x})} = -\mathbb{N}^{-1} \cdot \nabla \mathbf{e}^{-V_N(\mathbf{x})}. \quad (51)$$

Since the evaluation of u_N and v_N runs along parallel lines we now will use the symbol w_N to denote u_N or v_N , while W_N stands for the potentials U_N or V_N . Likewise, \mathbb{W} will be

the variable representing the matrices \mathbb{M} and \mathbb{N} . Using equations (50) and (51) we obtain for $w_N(i_1, \dots, i_K + 1, \dots, i_N)$

$$\begin{aligned}
 w_N(i_1, \dots, i_K + 1, \dots, i_N) &= \int_{\Omega_N} x_1^{i_1} \dots x_K^{i_K+1} \dots x_N^{i_N} e^{-W_N(x)} d^N x \\
 &= \int_{\Omega_N} x_1^{i_1} \dots x_K^{i_K} \dots x_N^{i_N} [x_K e^{-W_N(x)}] d^N x \\
 &= \int_{\Omega_N} x_1^{i_1} \dots x_N^{i_N} \left[- \sum_{L=1}^N \mathbb{W}_{KL}^{-1} \frac{\partial}{\partial x_L} e^{-W_N(x)} \right] d^N x \\
 &= \sum_{L=1}^N \mathbb{W}_{KL}^{-1} i_L \int_{\Omega_N} x_1^{i_1} \dots x_L^{i_L-1} \dots x_N^{i_N} e^{-W_N(x)} dx_1 \dots dx_N \\
 &\quad + \sum_{L=1}^N \mathbb{W}_{KL}^{-1} \delta_{i_L,0} \int_{\Omega_{N-1}} x_1^{i_1} \dots x_N^{i_N} e^{-W_N(x)} dx_1 \dots dx_{L-1} dx_{L+1} \dots dx_N \Big|_{x_L=0}.
 \end{aligned} \tag{52}$$

Due to the relation

$$W_N(x_1, \dots, x_L = 0, \dots, x_N) = V_{L-1}(x_1, \dots, x_{L-1}) W_{N-L}(x_{L+1}, \dots, x_N) \tag{53}$$

equation (52) can be written as

$$\begin{aligned}
 w_N(i_1, \dots, i_K + 1, \dots, i_N) &= \sum_{L=1}^N \mathbb{W}_{KL}^{-1} i_L w_N(i_1, \dots, i_L - 1, \dots, i_N) \\
 &\quad + \sum_{L=1}^N \mathbb{W}_{KL}^{-1} \delta_{i_L,0} v_{L-1}(i_1, \dots, i_{L-1}) w_{N-L}(i_{L+1}, \dots, i_N)
 \end{aligned} \tag{54}$$

where the ‘empty’ functions are to be understood as $w_0 = 1$. Note the explicit occurrence of the v -type moments in the formula for the w -type moments. This requires that the v -type moments have to be determined first. The above normalization constants in equations (39) and (41) are given by

$$Z_N^W = w_N(0, \dots, 0) \tag{55}$$

and serve as a starting point for a recursive determination of the higher-order moments according to the central relation, equation (54).

Having determined all relevant moments we can use them to obtain the matrix elements \mathbb{L}_{ij} and \mathbb{S}_{ij} :

$$\begin{aligned}
 \mathbb{L}_{ij} &= \langle \nabla_x \psi_{(i_1, \dots, i_N)}, \nabla_x \psi_{(j_1, \dots, j_N)} \rangle_{p_0} \\
 &= \frac{1}{Z_N^U} \sum_{K=1}^N i_K j_K \frac{u_N(i_1 + j_1, \dots, i_K + j_K - 2, \dots, i_N + j_N)}{c(i_1, \dots, i_N) c(j_1, \dots, j_N)}
 \end{aligned} \tag{56}$$

as well as

$$\begin{aligned}
 \mathbb{S}_{ij} &= \langle \psi_{(i_1, \dots, i_N)}, \psi_{(j_1, \dots, j_N)} \rangle_{p_0} - \langle \psi_{(i_1, \dots, i_N)} \rangle_{p_0} \langle \psi_{(j_1, \dots, j_N)} \rangle_{p_0} \\
 &= \frac{1}{Z_N^U} \frac{u_N(i_1 + j_1, \dots, i_N + j_N) - \frac{1}{Z_N^U} u_N(i_1, \dots, i_N) u_N(j_1, \dots, j_N)}{c(i_1, \dots, i_N) c(j_1, \dots, j_N)}.
 \end{aligned} \tag{57}$$

Finally, the eigenvalues and eigenvectors for the finite-dimensional approximations

$$\mathbb{L}^{(n)} v_i^{(n)} = \omega_i^{(n)} \mathbb{S}^{(n)} v_i^{(n)} \tag{58}$$

Table 1. Parameters for the numerical evaluation of the spectrum.

| Chain length N | Maximal degree for polynomials d_{\max} | Maximal number of basis functions n_{\max} | Number of matrix elements $\frac{n_{\max}(n_{\max}+1)}{2}$ | Required number of moments $\binom{N+2d_{\max}+1}{N}$ |
|---------------------|---|--|--|---|
| 2 | 15 | 106 | 5 671 | 528 |
| 3 | 14 | 402 | 81 003 | 4 960 |
| 4 | 13 | 984 | 484 620 | 31 465 |
| 5 | 12 | 1716 | 1 473 186 | 142 506 |
| 6 | 10 | 1405 | 987 715 | 296 010 |
| 7 | 8 | 749 | 280 875 | 346 104 |
| 8 | 7 | 552 | 152 628 | 490 314 |
| 9 | 6 | 345 | 59 685 | 497 420 |
| 10 | 5 | 175 | 15 400 | 352 716 |

of the original generalized eigenvalue problem, equation (21), are calculated numerically using standard NAG routines.

One should note that the approximating sequences are built successively by adding further basis functions. Hence, it is sufficient to determine $\mathbb{L}^{(n_{\max})}$ and $\mathbb{S}^{(n_{\max})}$ for some maximal dimension n_{\max} of the approximation. Any intermediate matrix $\mathbb{L}^{(n)}$ or $\mathbb{S}^{(n)}$ is then simply obtained by restricting the largest matrices to the corresponding n -dimensional upper-left submatrices. This feature even persists when equation (58) is transformed into a standard eigenvalue problem via a Cholesky decomposition of $\mathbb{S}^{(n)}$.

4. Discussion of the results

4.1. Numerical results

The numerical solution of equation (58) has been carried out for chains of lengths $N = 2$ – 10 . The maximal number of basis functions used and related parameters are listed in table 1. The size of the set of basis functions is restricted both by limitations of available memory and also by a loss of accuracy for the higher moments due to the number of recursion steps required for their computation. The number of recursions is given by $2d_{\max}$ of table 1, where d_{\max} denotes the maximal degree of the polynomials used as basis functions. For larger basis sets than those given in table 1, the diagonalization leads to negative eigenvalues, which is a sign for inherent numerical instabilities. Nevertheless, the relevant positive eigenvalues remain stable, and were checked for $N = 2$ and $N = 3$ by a direct evaluation of equations (46) and (47) for the moments.

Based on the parameters listed in table 1, we have determined numerically the eigenvalues and eigenvectors, as well as the end-to-end vector correlation functions. By varying the number of basis functions from $n = 20$ to $n = n_{\max}$ we have obtained information about the convergence, indicating that the physically relevant lower part of the spectrum is stable. A graphical illustration of the spectrum for a chain of length $N = 5$ is given in figure 2. The plots show the Rouse frequencies for:

- the free case, corresponding to the motion parallel to the surface;
- the mean-field approximation for the direction normal to the surface, to be discussed in the following section;
- the direction normal to the surface in the Rayleigh–Ritz approximation.

The frequencies are normalized with respect to the lowest fundamental Rouse frequency

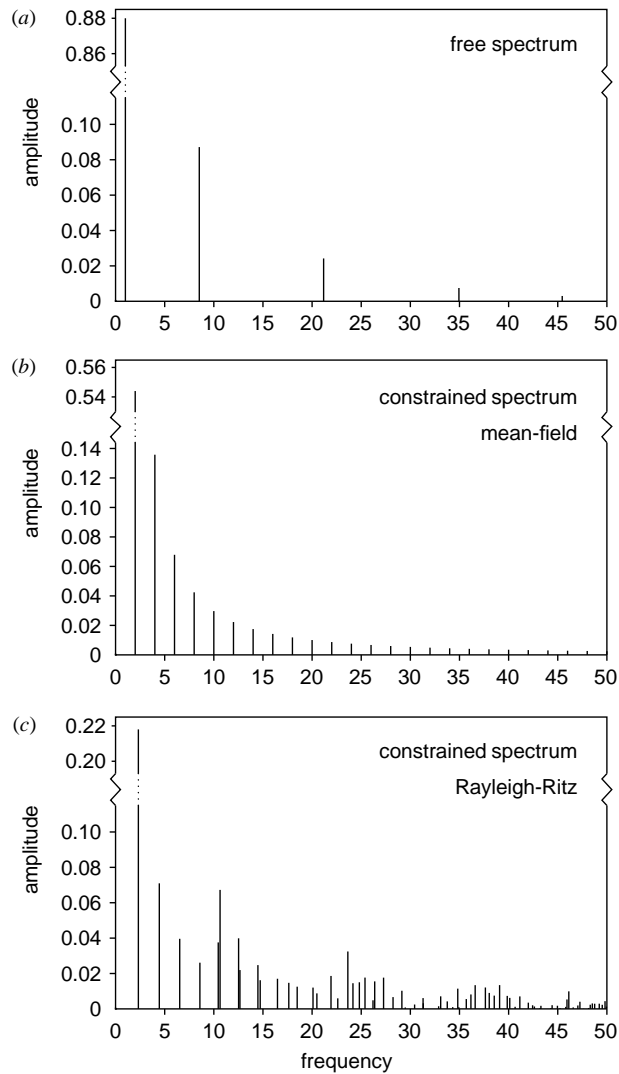


Figure 2. Relaxation spectra for a chain tethered to an impenetrable surface: (a) unconstrained motion (corresponding to the direction parallel to the surface); constrained dynamics (perpendicular to the surface), (b) in a mean-field approximation, (c) determined with the Rayleigh–Ritz scheme, see text for details.

of the free case, the amplitudes represent the contribution of the modes to the end-to-end correlation function.

Some important features can be read off from the numerical results:

- There is a frequency shift between parallel and normal relaxation.
- The mode picture is only approximately valid in the presence of the surface. Actually, the spectrum is no longer determined by the fundamental Rouse frequencies alone.
- Besides small distortions in the spectrum, anharmonicities make additional, non-negligible contributions to the correlation functions.

A significant quantity concerning the long-time behaviour of the dynamics may be

expressed in terms of the ratio of the lowest frequencies

$$s_N = \frac{\omega_{\min}^{\text{normal}}}{\omega_{\min}^{\text{parallel}}} \quad (59)$$

for the cases normal and parallel to the surface. These lowest frequencies are almost completely dominating the behaviour of the position autocorrelation function and its associated response functions. In particular, the response curves for the parallel and perpendicular case are essentially determined by their maxima near $\omega_{\min}^{\text{parallel}}$ and $\omega_{\min}^{\text{normal}}$, respectively. Some experiments yield a superposition of both response curves. The shift s_N then leads to a significant broadening of the total response curve, cf [13]. Beginning at $s_1 = 2$, the frequency shift s_N increases monotonically up to $s_N \simeq 2.4$ for large N . This result is also expected to be based on mean-field considerations, see section 4.2.

The second important feature of the spectrum are anharmonic effects. Note first that the eigenvalues are no longer regularly spaced. In particular, the spectrum for the relaxation normal to the surface is no longer determined by some small set of fundamental Rouse frequencies, since the problem is not separable and the modes of the free case are now coupled by reflections at the surface. Furthermore, all eigenvalues, and not only some subset of them leads to nonvanishing contributions to correlation functions. A simple physical interpretation of these results in terms of a mean-field approximation for the dynamics of the chain end is presented in section 4.2.

4.2. Interpretation in terms of a mean field picture

The numerical solution of the Fokker–Planck equation as given above is only tractable for N small enough. In the case of a continuous chain (N very large) an extension of the formalism is not immediate. As an alternative we use a mean-field approach to investigate the relaxation of a tethered, continuous chain. As in the discrete bead-spring model, we assume that the chain is fixed with one end to a planar surface. Furthermore, we concentrate on the chain's end-to-end vector.

Starting from the standard Gaussian model for continuous chains [2], we find that the equilibrium distribution for the free end of the tethered chain factors into a product of three independent parts, one for each spatial direction. The y - and z -parts parallel to the interface are Gaussian with mean zero and variance $\sigma_y^2 = \sigma_z^2 = \ell^2$, where ℓ denotes a suitable length scale of the model. The x -part—only defined for positive x —is an asymmetrical non-Gaussian distribution of the form (cf [17])

$$p_\ell(x) = \frac{x}{\ell^2} e^{-x^2/2\ell^2} \quad x \geq 0 \quad (60)$$

with mean-value and variance

$$\langle x \rangle_\ell = \sqrt{\frac{\pi}{2}} \ell \approx 1.25\ell \quad \sigma_x^2 = \frac{4 - \pi}{2} \ell^2 \approx \frac{1}{2.33} \ell^2. \quad (61)$$

Now, our basic assumption for the mean-field approximation is that the chain's end moves in an effective potential of the form

$$U_{\text{eff}}(\mathbf{r}) = -\ln p_\ell(\mathbf{r}). \quad (62)$$

As with the exact dynamics the corresponding time evolution is governed by the Fokker–Planck equation (7), now with the potential U_{eff} instead of U , again subject to Neumann boundary conditions at the surface. Using the Gaussian approximation instead of the actual

effective potential, we find that the characteristic relaxation times are proportional to the variances

$$\sigma_x^2 = \ell^2/2.33 \quad \text{and} \quad \sigma_y^2 = \sigma_z^2 = \ell^2. \quad (63)$$

Apart from these values, the behaviour is the same as for a fixed chain without any spatial constraints. In particular, only the corresponding fundamental relaxation frequencies yield contributions to linear correlation functions. Thus, anharmonicities are not present in such a crude Gaussian approximation, only the squeezing of the equilibrium distribution accompanied by a frequency shift

$$s_{\text{Gaussian}} = \frac{\sigma_y^2}{\sigma_x^2} = 2.33 \quad (64)$$

is captured.

An exact solution of the mean-field dynamics via eigenfunction expansion will overcome this failure of the simple Gaussian approximation. After a separation of variables corresponding to the different directions, we are left with Hermite equations for the parallel y - and z -directions, while the diffusion operator for the x -direction is of the form

$$\mathcal{L}_{\text{eff}}^{(x)} = -\frac{d^2}{dx^2} + \left[\frac{x}{\ell^2} - \frac{1}{x} \right] \frac{d}{dx}. \quad (65)$$

Applying the transformation $x \mapsto \zeta = \frac{x^2}{2\ell^2}$, the corresponding eigenvalue problem leads to the following confluent hypergeometric differential equation

$$\zeta \varphi'' + (1 - \zeta) \varphi' + \frac{\ell^2}{2} \omega \varphi = 0. \quad (66)$$

The solutions for this equation are the Laguerre functions $L_n(\zeta)$ with eigenvalues

$$\omega_n = \frac{2n}{\ell^2} \quad n = 0, 1, \dots \quad (67)$$

Resubstituting $\frac{x^2}{2\ell^2}$ for ζ , we find that these Laguerre functions automatically satisfy the Neumann boundary conditions. This effect is due to a total screening of the boundary by the effective potential, which shows an asymptotic behaviour of the form $U_{\text{eff}}(x) \sim \ln x$ for $x \rightarrow 0$.

At the level of the eigenvalues, the x -part of the spectrum is simply shifted by a factor of 2. In contrast to the above Gaussian approximation, however, there are nonvanishing contributions to the linear correlation functions from all parts of the spectrum, see figure 2.

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Appendix. The normalization constants Z_N^U and Z_N^V

The following derivation of Z_N^U and Z_N^V was communicated to us by Glasser [15], Clarkson University, Potsdam, New York, USA.

Let

$$I_N(t) = e^{-t^2} \int_{x_i \geq 0} \exp[-x_1^2 - (x_1 - x_2)^2 - \dots - (x_{N-1} - x_N)^2 - x_N^2 - 2x_N t] d^N x. \quad (68)$$

Then $I_N(0) = 2^{-N/2} Z_N^V$ and, by relabelling t as x_{N+1} ,

$$\int_0^\infty I_N(t) dt = \int_{x_i \geq 0} \exp[-x_1^2 - (x_1 - x_2)^2 - \dots - (x_N - x_{N+1})^2] d^{N+1}x \tag{69}$$

is the same as $2^{-(N+1)/2} Z_{N+1}^U$. Obviously, we have

$$I_{N+1}(t) = \int_0^\infty e^{-(t-u)^2} I_N(u) du. \tag{70}$$

Now let G be the generating function:

$$G(t) = \sum_{N=0}^\infty I_N(t) z^N \quad |z| < 1. \tag{71}$$

It is easy to see that $G(t)$ satisfies the integral equation

$$G(t) = e^{-t^2} + z \int_0^\infty e^{-(t-u)^2} G(u) du \tag{72}$$

which can be solved by the Wiener–Hopf method. Note that $I_N(t)$ is bounded for positive t and is exponentially small for negative t , so the same is true of $G(t)$. In the usual notation the integral equation is:

$$G_+(t) + G_-(t) = e^{-t^2} + z \int_{-\infty}^\infty e^{-(t-u)^2} G_+(u) du. \tag{73}$$

Its Fourier transform, by the convolution theorem, is

$$\hat{G}_+(\omega) + \hat{G}_-(\omega) = \sqrt{\pi} e^{-(\omega/2)^2} [1 + z \hat{G}_+(\omega)]. \tag{74}$$

Now, $\hat{G}_+(\omega)$ is analytic in the upper half ω -plane and $\hat{G}_-(\omega)$ is an entire function. Let

$$g(\omega) = 1 - \sqrt{\pi} z e^{-(\omega/2)^2} \tag{75}$$

which is nonzero in ‘the strip’ $-\nu < \text{Im } \omega < \nu$, where $\nu = 2|\ln(\sqrt{\pi}z)|^{1/2}$. It has the Wiener–Hopf factorization

$$g(\omega) = \frac{g_+(\omega)}{g_-(\omega)} \tag{76}$$

$$g_\pm(\omega) = \exp \left[\frac{1}{2\pi i} \int_{-\infty + ia_\pm}^{\infty + ia_\pm} \frac{\ln g(u)}{u - \omega} du \right] \tag{77}$$

for $-\nu < a_+ < a_- < \nu$. Therefore, in the strip we have

$$g_+(\omega) \left[\hat{G}_+(\omega) + \frac{1}{z} \right] = -g_-(\omega) \left[\hat{G}_-(\omega) - \frac{1}{z} \right]. \tag{78}$$

Since the LHS is analytic in the strip and above, and the RHS is analytic in the strip and below, both sides must be the same entire function $\psi(\omega)$. Since $g_+(\omega) \rightarrow 1$ as $|\omega| \rightarrow \infty$ and $\hat{G}_+(\omega) \rightarrow 0$, by Liouville’s theorem $\psi(\omega) = 1/z$. Thus

$$\hat{G}_+(\omega) = \frac{1}{z} \left\{ \exp \left[\int_{-\infty}^\infty \frac{\ln g(u)}{\omega - u} \frac{du}{2\pi i} \right] - 1 \right\}. \tag{79}$$

Now we have

$$\sum_{N=1}^\infty (z/\sqrt{2})^N Z_N^U = z \int_0^\infty G(t) dt = z \hat{G}_+(0) \tag{80}$$

with

$$\hat{G}_+(0) = \lim_{\eta \rightarrow 0^+} \hat{G}_+(i\eta). \quad (81)$$

By the formula $(u - i\eta)^{-1} = \mathcal{P}_u^{-1} + i\pi\delta(u)$,

$$z\hat{G}_+(0) = \frac{1}{\sqrt{1 - z\sqrt{\pi}}} - 1 = \sum_{N=1}^{\infty} \frac{1}{N!} \frac{1}{2^N} (z\sqrt{\pi})^N \quad (82)$$

so $Z_N^U = (2\pi)^{N/2} \frac{1}{N!}$. Next,

$$\sum_{N=0}^{\infty} (z/\sqrt{2})^N Z_N^V = G(0). \quad (83)$$

But, by Watson's lemma

$$\int_0^{\infty} G(u)e^{iu\omega} du = \hat{G}_+(\omega) \sim \frac{iG(0)}{\omega} \quad (84)$$

and for large ω

$$\hat{G}_+(\omega) \sim \frac{1}{2\pi i\omega z} \int_{-\infty}^{\infty} \ln(1 - \sqrt{\pi}ze^{-(u/2)^2}) du \quad (85)$$

so

$$\begin{aligned} G(0) &= -\frac{1}{\pi z} \int_0^{\infty} \ln(1 - \sqrt{\pi}ze^{-(u/2)^2}) du \\ &= \frac{1}{\pi z} \sum_{N=1}^{\infty} \frac{(z\sqrt{\pi})^N}{n} \int_0^{\infty} e^{-nu^2/4} du = \sum_{N=0}^{\infty} \frac{(z\sqrt{\pi})^N}{(N+1)^{3/2}}. \end{aligned} \quad (86)$$

Hence $Z_N^V = (2\pi)^{N/2} (N+1)^{-3/2}$.

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