Constrained dynamics of a polymer ring enclosing a constant area

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The dynamics of an ideal polymer ring enclosing a constant *algebraic* area is studied. The constraint of a constant area is found to couple the dynamics of the two Cartesian components of the position vector of the polymer ring through the Lagrange multiplier function which is time dependent. The time dependence of the Lagrange multiplier is evaluated in a closed form both at short and long times. At long times, the time dependence is weak, and is mainly governed by the inverse of the first mode of the area. The presence of the constraint changes the nature of the relaxation of the internal modes. The time correlation of the position vectors of the ring is found to be dominated by the first Rouse mode which does not relax even at very long times. The mean square displacement of the radius vector is found to be diffusive, which is associated with the rotational diffusion of the ring.

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I. INTRODUCTION

The equilibrium statistics of a planar Brownian motion enclosing a constant area was first studied by Lévy in 1940 with a view to obtain the probability distribution function for the *algebraic* area [1,2]. A simple analogy to topologically constrained (entangled) polymers, which can approximately be represented by a planar random walk constrained to enclose a constant area, was later pointed out by Brereton and Butler [3]. To describe the configurational and mechanical properties of these polymers, they readdressed this problem using discrete Gaussian chains. An exact expression for the probability distribution function was subsequently obtained using continuous models for Gaussian chains [4,5].

Most of the studies on constrained polymer rings have been restricted to static equilibrium behavior. However, the dynamics of a polymer ring constrained to enclose a constant area can serve as a useful model in several different areas of statistical physics. The Rouse dynamics of a highly dense ensemble of long polymer chains, in general, is a simple and well known example of the constrained dynamics due to the presence of entanglements. The highly nonlocal nature of these constraints renders the analytical solution of the problem difficult. Therefore, the dynamics of polymer melts is mainly studied by phenomenological tube models [6] and their extensions [7]. For a polymer ring, on the other hand, analogies with topologically constrained loops can be realized at a more formal level [3]. The mathematical formulation of the constant area constraint is strongly related, for instance, to the Gaussian invariance of the entangled loops [6], and topological problems concerning the writhe of a polymer ring [8]. Some connections with rings enclosing topological obstacles can also be discussed within a similar framework [9].

As another instance, a self-avoiding polymer ring enclosing a two-dimensional volume is a simple model to describe the equilibrium properties of two-dimensional vesicles [10]. A finite pressure differential between the interior and exterior of the one-dimensional membrane keeps the enclosed area constant. As a result two-dimensional vesicles can be modeled both in the constant pressure and constant-area ensembles. The static equilibrium studies in these two ensembles were carried out by Rudnick and Gaspari, where two-dimensional vesicles were described using "pressurized" random walks [11]. Although the effects due to self-avoidance were completely neglected, the latter studies compared well with the scaling predictions of the numerical studies by Leibler *et al.* [10] in certain regimes. The dynamics of a polymer ring (closed random walk) enclosing a constant area can, therefore, be regarded as a very simple (zeroth-order) model to describe the dynamics of a two-dimensional vesicle bounded by a one-dimensional lipid membrane, the perimeter of which undergoes randomly kicked motion due to the stochastic thermal forces from the solvent; the osmotic pressure difference between the two sides of the membrane keeps the area constant at all times. It is more appropriate to describe the dynamics of vesicles in the constant-area ensemble since vesicles, when subjected to Brownian motion, do not undergo volume change, i.e., area change in two dimensions. The constraint of constant area can be enforced by introducing a time dependent Lagrange multiplier in the stochastic equations for a polymer ring. The Lagrange multiplier, therefore, plays the role of the time dependent differential pressure, the dynamics of which ensures that the area is constant at all times.

The technical difficulties involved in treating the constrained dynamics of a polymer ring arise from the global nature of the area constraint. Additionally, since the constraint of a constant area has to be satisfied at each time t, the dynamical behavior of the two Cartesian components of a spatial vector $\mathbf{r}(s,t)=[r_x(s,t),r_y(s,t)]$ at any point s along the curve are no longer independent—the rigid constraint of a constant area strongly couples the two coordinates through the Lagrange multiplier. The time dependence of the latter makes the analytical solution of the stochastic equations difficult.

In a more general context, the present problem belongs to the comparatively less understood field of stochastic dynamics with rigid constraints. Even in a more specific case of the dynamics of polymers with rigid constraints, the literature is mainly restricted to the Kirkwood theory for hydrodynamics

and the dynamics of semiflexible polymers [6]. One reason for the limited literature on such systems is the technical difficulty involved in dealing with dynamical problems with rigid constraints. The nature of the difficulty become apparent in the field-theoretic formulation of the dynamical problem, where the presence of any constraint changes the number of dynamical variables and adds the Lagrange multiplier to the set of variables. Any functional formulation of the dynamics of the constrained system is, therefore, altered by an additional Jacobian, which is difficult to determine. In some cases the introduction of noncommuting Grassmann variables can facilitate a solution [12]. For the present problem, however, we show that the nature of the area constraint is such that a simple Langevin description suffices and a field-theoretic formulation is not necessary.

Within the Langevin description, the area constraint is accounted for by the Lagrange multiplier function which is time dependent. The time dependence of the Lagrange multiplier can be calculated in a closed form (which is quite unusual for the problems of this nature) for an initial perturbation of the area modes and allows us to solve the coupled stochastic equations for the polymer ring. It is shown that the dynamics of a polymer ring enclosing constant area is mainly governed by the lowest Rouse mode. The constraint of a constant area is fixed by the first Rouse mode (associated with rotation [6]), which is found to be diffusive at long times. The present problem is a simple and well chosen example to describe several interesting aspects of stochastic dynamics with rigid constraints.

II. MODEL

Let us first introduce the model we are going to study and review some of the static results. The algebraic area enclosed by a planar random walk in a continuous representation is defined by

$$A[\mathbf{r}(s,t)] = \frac{1}{2}\int_0^N ds\left(\mathbf{r}(s,t) \times \frac{\partial \mathbf{r}(s,t)}{\partial s}\right)\cdot \mathbf{k}, \tag{1}$$

where $\mathbf{k}$ is the unit vector perpendicular to the (x,y) plane; $\mathbf{r}(s,t)$ is the position vector starting from the center of mass of the chain (placed at the origin) to the segment s along a chain of contour length N, which for a ring satisfies $\mathbf{r}(N,t) = \mathbf{r}(0,t)$. In statics, the constraint of a constant area is imposed by including a delta function $\delta(A\{\mathbf{r}\}-A)$ in the partition function such that the probability distribution function for A is given by

$$P(A,N) = \mathcal{N}\int_{\mathbf{r}_0,0}^{\mathbf{r}_0,N} \mathcal{D}[\mathbf{r}(s)]\delta(A\{\mathbf{r}\}-A) \times \exp\left[-\frac{1}{b^2}\int_0^N ds\left(\frac{\partial \mathbf{r}(s)}{\partial s}\right)^2\right], \tag{2}$$

where $\mathcal{N}$ is the normalization constant and b is the segment length; the term in the exponential is the Wiener measure which accounts for the entropic elasticity of the polymer. The area constraint restricts the conformations of a polymer ring in such a way that closed random walks of only a given constant area A contribute to the partition function. Since the sign of the area [as defined by Eq. (1)] depends on the orientation of the contour, the constraint restricts the magnitude of the area but has no control over the shape of a ring. The latter implies that a symmetric "figure of eight" has an *algebraic* area zero and a random walk (Gaussian chain) with a large number of wiggles along its contour length will undergo many cancellations to keep the average area constant [3].

The delta function in Eq. (2) can be Fourier transformed, i.e., $\delta(A\{\mathbf{r}\}-A) = \int dg \exp[ig(A\{\mathbf{r}\}-A)]$, such that g is a variable conjugate to A. The probability distribution $P(A,N)$ can then be determined for a discrete closed random walk using normal mode analysis [3] or its continuous representation using functional integration [4,5]; it is given by $P(A,N) = [2Nb^2\cosh^2(2\pi A/Nb^2)]^{-1}$, which has the asymptotic behavior of $\exp(-4\pi A/Nb^2)$ for $A/Nb^2 \gg 1$.

The constrained dynamics of a constant area can be treated by the method of Lagrange multipliers [6]; the idea is to add the constraining force explicitly in the Langevin equation. The constraint of a constant area when introduced using a Lagrange multiplier function $\lambda(t)$ produces a coupling between x and y coordinates. The coupled Langevin equations are given by

$$\zeta\frac{\partial r_x(s,t)}{\partial t} = \frac{2k_BT}{b^2}\frac{\partial^2 r_x(s,t)}{\partial s^2} + k_BT\lambda(t)\frac{\partial r_y(s,t)}{\partial s} + f_x(s,t), \tag{3}$$

$$\zeta\frac{\partial r_y(s,t)}{\partial t} = \frac{2k_BT}{b^2}\frac{\partial^2 r_y(s,t)}{\partial s^2} - k_BT\lambda(t)\frac{\partial r_x(s,t)}{\partial s} + f_y(s,t), \tag{4}$$

where the first term in the above equations represents dissipation due to the viscous forces of the solvent with friction coefficient ζ; f is the fluctuating force whose time average is zero. The dissipation and the fluctuations are related to each other by the simplest form of the fluctuation dissipation theorem which dictates $\langle f_i(s,t)f_j(s',t')\rangle = 2\zeta k_BT\delta_{ij}\delta(s-s')\delta(t-t')$. The second term represents the elastic force due to the chain connectivity. The coupling shows the most trivial effect of the constraint: the dynamics of the two components $r_x(s,t)$ and $r_y(s,t)$ is no longer independent, as is the case in the absence of constraint.

In terms of the normal modes, i.e., $\mathbf{r}_p(t) = (1/N)\int_0^N ds\, \mathbf{r}(s,t)e^{2ip\pi s/N}$, Eqs. (3) and (4) can be rewritten as

$$\zeta_p\frac{dr_{px}(t)}{dt} = -kp^2 r_{px}(t) - 2ip\pi k_BT\lambda(t)r_{py}(t) + f_{px}(t), \tag{5}$$

$$\zeta_p\frac{dr_{py}(t)}{dt} = -kp^2 r_{py}(t) + 2ip\pi k_BT\lambda(t)r_{px}(t) + f_{py}(t), \tag{6}$$

where $k = 8\pi^2 k_BT/Nb^2$, $\zeta_0 = N\zeta$ and $\zeta_{p\neq 0} = 2N\zeta$ [6]. $A(t) = \sum_{p=-\infty}^{\infty}(-ip\pi)A_p(t)$, where

$$A_p(t) = r_{px}(t)r_{-py}(t) - r_{py}(t)r_{-px}(t). \tag{7}$$

A more compact vectorial representation of the set of coupled Langevin equations can be presented by using a matrix notation,

$$\zeta_p \frac{d}{dt}\mathbf{r}_p(t) = -k_B T \mathbf{M}_p(t)\cdot \mathbf{r}_p(t) + \mathbf{f}_p(t), \tag{8}$$

where the matrix $\mathbf{M}_p(t)$ is defined

$$\mathbf{M}_p(t) = \begin{pmatrix} 8p^2\pi^2/(Nb^2) & 2ip\pi\lambda(t) \\ -2ip\pi\lambda(t) & 8p^2\pi^2/(Nb^2) \end{pmatrix}, \tag{9}$$

whose eigenvalues ℓ_e are given by

$$\ell_e = 8p^2\pi^2/(Nb^2) \pm 2p\pi\lambda(t), \tag{10}$$

which correspond to the relaxation of the individual Rouse modes of the chain the details of which will be discussed later.

Since the area constraint is local in time t but global in the contour length s, the Lagrange multiplier λ depends only on time. The time dependence of Lagrange multiplier makes the exact solution of the coupled Langevin equations difficult. Any exact or approximate solution requires a complete knowledge of the time dependence of $\lambda(t)$. Since the dynamics of $\lambda(t)$ has to be such that the area $A(t)$ has to be constant at all times, we begin by writing down the equation of motion for the area modes itself, the details of which are presented below.

III. AREA CONSERVATION

A. Dynamics of mode-dependent area

To get a dynamical equation for the area of a polymer ring, we add and subtract the imaginary part of Eq. (6) from Eq. (5) in such a way that we get dynamical equations for $(r_{px}+ir_{py})$ and $(r_{-px}-ir_{-py})$.

A series of simple steps will provide a stochastic (Langevin type) equation for area: multiply the dynamical equation for $(r_{px}+ir_{py})$ by $(r_{-px}-ir_{-py})$ (that is its complex conjugate) and $(r_{-px}-ir_{-py})$ by $(r_{px}+ir_{py})$; after having added the two equations, separate the real and the imaginary parts of the resulting equation, which for $p\neq 0$ modes are given by the following expressions respectively:

$$\zeta_p \frac{dr_p^2(t)}{dt} = -[2kp^2 + 4p\pi k_B T\lambda(t)]r_p^2(t), \tag{11}$$

$$\zeta_p \frac{dA_p(t)}{dt} = -[2kp^2 + 4p\pi k_B T\lambda(t)]A_p(t), \tag{12}$$

where $A_p(t)$ is given by Eq. (7) and $r_p^2(t)=r_{px}(t)r_{-px}(t)+r_{py}(t)r_{-py}(t)$. It is not surprising that the above two equations have a similar structure since the first one represents the radius and the second one the area of the pth mode of the ring. To get the time dependence of $\lambda(t)$, we are interested in the time development of the average of $A_p(t)$, which in thermal equilibrium is time independent. Therefore, in writing the dynamical equation for $A_p(t)$, we have implicitly assumed an average over a nonequilibrium ensemble in which $\langle A_p(t)\rangle_{neq}$ is explicitly time dependent. This gives us the dynamical response of the Lagrange multiplier to a perturbation of the area modes away from their thermal equilibrium values [13].

The area conservation demands $dA(t)/dt = \Sigma_p(-ip\pi)dA_p(t)/dt = 0$. This constraint when used in Eq. (12) produces the following expression for the Lagrange multiplier:

$$\lambda(t) = -\frac{4\pi}{Nb^2}\frac{\sum_p p^3 A_p(t)}{\sum_p p^2 A_p(t)}, \tag{13}$$

where $Nb^2/4\pi$ is the area of the first mode; it corresponds to a random walk which on an average forms a circle. For a random walk to form a circle in an average sense, the circumference $2\pi r$ should be equal to $N^{1/2}b$, where r is the radius of the circle; this condition determines $r=N^{1/2}b/2\pi$. Thus, the area of the circle on an average turns out to be $Nb^2/4\pi$. The second mode is a symmetric figure of eight and so on.

The time dependence of the Lagrange multiplier can be determined in a self-consistent way. To begin with we consider $\lambda(t)$ to be independent of time and given by $-4\pi/Nb^2$. This approximation amounts to solving Eq. (12), which is a simple first-order differential equation in time, and can be easily solved to produce $A_p(t)=A_p(0)\exp(-t/\tau_p)$, where τ_p is the relaxation time of the pth mode given by $\tau_p = N^2b^2\zeta/[8\pi^2k_BTp(p-1)]$. The latter implies that all modes except the first one, which has a constant area $A_1(0)$, decay with the relaxation time of τ_p. The same is true for the radius of the pth mode.

We can now substitute the expression for $A_p(t)$ into Eq. (13) to see how $\lambda(t)$ evolves with time. In the limiting case of $\lambda(t\to\infty)=-4\pi/Nb^2$, the dominance of the first mode is evident. The latter is true for all times greater than the relaxation time $\tau=N^2b^2\zeta/[8\pi^2k_BT]$. It is clear from Eq. (13) that for all times $t\ll\tau$, the dynamics is determined by the summation over large number of modes; for times $t\gg\tau$, on the other hand, the dynamics is dominated by the first mode. Thus, the dynamics of $\lambda(t)$ is reflected in its dependence on p modes, which decays in time in such a way that for $t\gg\tau$ it is only determined by $p=1$.

To get an idea of the time dependence for times much less than the relaxation time τ, one can replace the summation by an integration over p modes in Eq. (12). In the limit of $t\ll\tau$, the time dependence of the Lagrange multiplier is approximately given by $\lambda(t)\approx -4\pi/Nb^2(\tau/t)^{1/2}$. It is to be noted that in carrying out the integration over the modes, we have neglected the p dependence of $A_p(0)$. The mode dependence of $A_p(0)$, however, does not alter the way $\lambda(t)$ scales with t. At short times, the nature of the decay of the pth mode is reflected in the time dependence of $\lambda(t)$. It is evident from the expression for $A_p(t)$ that for $t\gg\tau/p^2$, the pth mode has already relaxed and does not contribute to the summation in Eq. (13). This implies that the number of modes that contribute to the summation in Eq. (13) at any time t are approximately given by $p^*(t)\approx(\tau/t)^{1/2}$. The algebraic time de-

pendence of $\lambda(t)$ can easily be found from Eq. (12). If it is assumed that in this time regime some modes have already relaxed, then $dA_{p^*}/dt=0$ for these modes. Then the solution for the Langrange multiplier $\lambda(t)$ is approximately given by

$$\lambda(t) \simeq -\frac{4\pi}{Nb^2}p^*. \tag{14}$$

Since the modes follow the Rouse relaxation, the inverse square root time dependence of $\lambda(t)$ can be understood.

The time dependent expression for $\lambda(t)$ when substituted into Eq. (12) yields $A_p(t) \approx A_p(0)e^{-p^2t/\tau}e^{p(t/\tau)^{1/2}}$, which at short times is a stretched exponential. The latter implies that for time $t \ll \tau$, the constraint of constant area affects the dynamics of $A_p(t)$ in such a way that the lower modes grow at the expense of the higher ones leaving the total area constant; for time $t \gg \tau$ only the first mode, which attains a constant value, survives. In contrast, the dynamics of $\lambda(t)$ is such that it decays in time as $(\tau/t)^{1/2}$ and at $t \gg \tau$ attains a constant value of $-4\pi/Nb^2$.

This gives us an idea about the dynamics of $\lambda(t)$, which for all times $t \gg \tau$, is weakly dependent on time and is mainly dominated by the first mode. In what follows, we will replace $\lambda(t)$ by a time independent quantity λ_0 to discuss the statics of a closed random walk.

B. Statics

To recover some of the equilibrium results of the earlier studies from dynamics, we begin by introducing temporal Fourier transform into Eqs. (5) and (6):

$$-i\omega\zeta_p r_{px}(\omega) = -kp^2 r_{px}(\omega) - 2ip\pi\lambda_0 k_B T r_{py}(\omega) + f_{px}(\omega), \tag{15}$$

$$-i\omega\zeta_p r_{py}(\omega) = -kp^2 r_{py}(\omega) + 2ip\pi\lambda_0 k_B T r_{px}(\omega) + f_{py}(\omega). \tag{16}$$

The resulting coupled equation can be easily be solved to calculate the following correlation:

$$\langle \mathbf{r}_p(\omega)\cdot\mathbf{r}_{-p}(-\omega)\rangle = 2k_BT\zeta_p\left(\frac{1}{[\zeta_p^2\omega^2 + (kp^2 - 2p\pi k_BT\lambda_0)^2]} + \frac{1}{[\zeta_p^2\omega^2 + (kp^2 + 2p\pi k_BT\lambda_0)^2]}\right), \tag{17}$$

where the angular brackets represent an average with respect to the random noise. To calculate the equal time correlation we use $\langle r_{pi}r_{-pj}\rangle = \int(d\omega/2\pi)\langle r_{pi}(\omega)r_{-pj}(-\omega)\rangle$; the resulting expression is given by

$$\langle \mathbf{r}_p(t)\cdot\mathbf{r}_{-p}(t)\rangle = \frac{Nb^2/2}{(p^2\pi^2 - \lambda_0^2N^2b^4/16)}. \tag{18}$$

The mean square distance of a chord starting from $\mathbf{r}(0)$ and ending at any point s along the chain contour is defined by $\mathbf{R}^2(s)=[\mathbf{r}(s)-\mathbf{r}(0)]^2$. In terms of the normal modes it is given by $\mathbf{R}^2(s)=4\Sigma_{p=1}^{\infty}(\mathbf{r}_p\cdot\mathbf{r}_{-p})\sin^2(p\pi s/N)$. In the limit of $N\to\infty$ and $p\pi/N\to q$, the summation can be converted to an integral to give

$$\mathbf{R}^2(s) = 2b^2/\pi\int_0^\infty dq\,\sin^2(qs)/(q^2 + g^2b^4/16), \tag{19}$$

which is the same as Eq. (5.3) in the paper by Brereton and Butler [3]. In writing the above expression we have taken $\lambda_0 = ig$ such that the integral can be done by contour integration; it has double poles in the complex g plane given by $g = \pm 4iq/b^2$ [3]. The latter implies that when $q=p\pi/N$, the Lagrange multiplier is given by $\lambda_0 = \pm 4p\pi/Nb^2$.

The integral in Eq. (19) can easily be evaluated and Fourier transformed with respect to g; the result can be averaged over the equilibrium probability distribution given by $P(A) = \exp(-4\pi A/Nb^2)$ to give the following expression:

$$\langle \mathbf{R}^2(s)\rangle_A = \frac{Nb^2}{2}(1+\alpha^2)\ln\left(\frac{\alpha^2 + (1+s/N)^2}{\alpha^2+1}\right), \tag{20}$$

where $\alpha = 2A/Nb^2$. It is interesting to note that in equilibrium the probability distribution, which yields $\langle A\rangle = Nb^2/4\pi$, imposes the dominance of the first mode over all other modes. In essence it means that the presence of the area constraint introduces significant deviations from the unperturbed random walk for $A/Nb^2 \gg 1$; in the latter limit the mean square distance is given by $\langle \mathbf{R}^2(s)\rangle_A \approx sb^2(1+s/N)^2/2$.

C. Dynamics of a Gaussian chain

As discussed in Sec. III, the dynamics of the Lagrange multiplier function $\lambda(t)$, when calculated in a self-consistent way, suggests its inverse dependence on the first mode of the area, i.e., $-4\pi/Nb^2$. The latter expression when substituted into Eqs. (15) and (16) produces coupled equations in $r_p(x)$ and $r_p(y)$, which can easily be solved to give

$$\langle \mathbf{r}_p(\omega)\cdot\mathbf{r}_{-p}(-\omega)\rangle = 2k_BT\zeta_p\left(\frac{1}{[\zeta_p^2\omega^2 + (k^2p^2(p+1)^2]} + \frac{1}{[\zeta_p^2\omega^2 + k^2p^2(p-1)^2]}\right). \tag{21}$$

The time-correlation function can be calculated using $\langle \mathbf{r}_p(t)\cdot\mathbf{r}_{-p}(0)\rangle = \int(d\omega/2\pi)\langle \mathbf{r}_p(\omega)\cdot\mathbf{r}_{-p}(-\omega)\rangle e^{i\omega t}$. For $p=1$ mode the correlation function is given by

$$\langle \mathbf{r}_1(t)\cdot\mathbf{r}_{-1}(t')\rangle = \frac{Nb^2}{16\pi^2}\exp\left(-\frac{8\pi^2k_BT|t-t'|}{N^2b^2\zeta}\right) + \frac{k_BT|t-t'|}{N\zeta}. \tag{22}$$

For $p\neq 1$ modes, on the other hand, the time-correlation function is given by

$$\langle \mathbf{r}_p(t)\cdot\mathbf{r}_{-p}(t')\rangle = \frac{Nb^2}{4\pi^2(p^2-1)}\exp\left(-\frac{4\pi^2p^2k_BT|t-t'|}{N^2b^2\zeta}\right)\times\left[\cosh\left(\frac{4\pi^2pk_BT|t-t'|}{N^2b^2\zeta}\right) + \frac{1}{p}\sinh\left(\frac{4\pi^2pk_BT|t-t'|}{N^2b^2\zeta}\right)\right]. \tag{23}$$

The radius of the ring at any point s along the curve is given

by $\mathbf{R}(s,t)=\mathbf{r}(s,t)-\mathbf{r}_0(t)$, where $\mathbf{r}_0(t)$ is the position of the center of mass at time t defined as $\mathbf{r}_0(t)=(1/N)\int_0^N ds\mathbf{r}(s,t)$. The time correlation of the radii at two different times in terms of the normal modes is given by $\langle \mathbf{R}(s,t)\cdot\mathbf{R}(s,t')\rangle = 4\Sigma_{p=1}^{\infty}\langle \mathbf{r}_p(t)\cdot\mathbf{r}_{-p}(t')\rangle$. Since the relaxation time associated with the first mode, that is $\tau=N^2b^2\zeta/8\pi^2k_BT$, is the longest relaxation time of the correlation function, it corresponds to the rotational relaxation time [6]. For all times greater than the relaxation time, that is $t\gg\tau$, the dynamics is dominated by the first Rouse mode, which is diffusive. The mean square displacement of the radius $\mathbf{R}(N,t)$ is given by

$$\langle[\mathbf{R}(N,t)-\mathbf{R}(N,0)]^2\rangle = \frac{8k_BTt}{N\zeta}, \tag{24}$$

where at long times it corresponds to the rotational diffusion of the ring; the rotational diffusion constant is given by $D_{\mathrm{rot}}=2k_BT/N\zeta$. The mean square displacement of the center of mass, on the other hand, is estimated by the $p=0$ mode, i.e., $\langle[\mathbf{r}_0(t)-\mathbf{r}_0(0)]^2\rangle=4k_BTt/(N\zeta)$, at long times the self-diffusion constant of the center of mass of the ring is given by $D_0=k_BT/N\zeta$ [6]. The rotational diffusion constant is, therefore, twice of the diffusion constant of the center of mass of the ring. It is not surprising, however, that both the diffusion constants have Rouse type scaling since in both cases the the friction coefficient is determined by the Rouse friction $N\zeta$. The diffusion constants for the $p=0$ diffusion and the area preserving $p=1$ rotation must, therefore, have the same Rouse type scaling.

Since the area constraint couples the x and y modes, the cross correlations, i.e., $\langle r_{px}(t)r_{-py}(t')\rangle$, turn out to be nonzero. The equal time correlation amounts to estimating the average of $A_p(t)$, which can easily be evaluated using Eq. (7). The summation over p modes defines the average area, which is given by $\langle A(t)\rangle=Nb^2/4\pi$.

The dominance of the diffusive first mode has been seen in a very different context of grafted polymer brushes [14]. In the latter study the distribution of the chain ends is accounted for by self-consistent-field theory which determines the mean-field potential seen by each monomer self-consistently [15]. In dynamics it amounts to the dominance of the first mode, which does not relax, and is associated with the diffusion of the chain end in brushes. In the present study although the imposition of area constraint through the time dependent Lagrange multiplier and its determination from the dynamical equations is of very different nature, the dominance of the first (Rouse) mode, as also seen in the dynamics of polymer brushes, is interesting.

D. Dynamics of a self-avoiding chain

So far our study has been restricted to understanding the dynamics of a Gaussian chain (random walk) constrained to enclose a constant algebraic area, which is represented by a complex loop in Fig. 1. To address the more realistic case of a self-avoiding chain enclosing a constant area (simple loop in Fig. 1), we need to account for the excluded volume interactions through an additional potential, $U=\frac{1}{2}vk_BT\int_0^N ds\int_0^N ds'\,\delta[\mathbf{r}(s,t)-\mathbf{r}(s',t)]$, in the chain Hamiltonian. However, the inclusion of such a potential makes the resulting dynamical equations nonlinear and difficult to treat analytically.

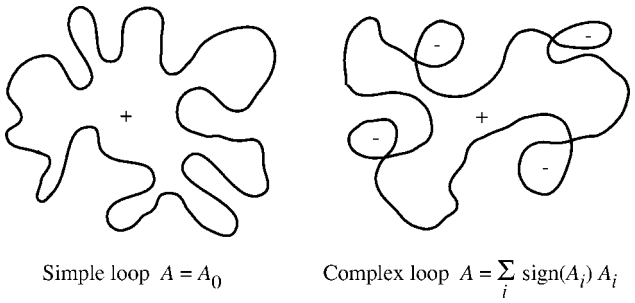

FIG. 1. A schematic representation of a simple and complex loop depicting the *algebraic* area enclosed by a closed self-avoiding and random walk, respectively. The positive and negative signs denote the orientation of the contour.

Although the excluded volume interactions are conceptually important to the present problem, they do not change the basic ideas of the Gaussian theory. The main reason for this can be seen in the nature of the area constraint itself, which does not couple to the densities. In particular, the area constraint leads to terms which are given by the Cartesian components of the chain vector itself and the bond vector, i.e., the derivative of the chain vector with respect to the contour variable s. This implies that the constraint does not couple to the excluded volume interaction (given by the square of the local density). Therefore, a simple linearization approximation accounts for the excluded volume interactions in an effective way [6], and includes the excluded volume effects in the parameter k_p of Eqs. (5) and (6), which is given by $k_p \approx k_BTp^{1+2\nu}/N^{2\nu}b^2$, where $\nu=3/5$ for a self-avoiding chain; the first term on the right-hand side of Eqs. (5) and (6) containing p^2 is replaced by $p^{1+2\nu}$.

A similar analysis shows that within the linearized approximation the presence of the effective excluded volume interactions changes the nature of the mode relaxation. At long times, the first mode of the area remains constant, but all other modes decay as $A_p(t)\approx A_p(0)\exp[-p(p^{2\nu}-1)t/\tau]$, where $\tau\approx N^{2\nu+1}b^2\zeta/k_BT$. $\lambda(t)$, on the other hand, is given by $\lambda(t)\approx -1/N^{2\nu}b^2$. For all times $t\ll\tau$, $A_p(t)\approx A_p(0)\exp(-p^{2\nu+1}t/\tau)\exp[-p(t/\tau)^{1/1+2\nu}]$ and $\lambda(t)\approx -(t/\tau)^{-2\nu/(1+2\nu)}$.

At long times the time correlation of all modes except the first one, which is diffusive, is given by

$$\langle \mathbf{r}_p(t)\cdot\mathbf{r}_{-p}(t')\rangle \approx \frac{N^{2\nu}b^2p^{2\nu-1}}{(p^{4\nu}-1)}\exp\left(-\frac{p^{2\nu+1}k_BT|t-t'|}{N^{2\nu+1}b^2\zeta}\right) \times\left[\cosh\left(\frac{pk_BT|t-t'|}{N^{2\nu+1}b^2\zeta}\right) + \frac{1}{p^{2\nu}}\sinh\left(\frac{4\pi^2pk_BT|t-t'|}{N^{2\nu+1}b^2\zeta}\right)\right]. \tag{25}$$

The mean square displacement of the radius $\mathbf{R}(N,t)$ is still diffusive and scales as $\langle[\mathbf{R}(N,t)-\mathbf{R}(N,0)]^2\rangle\approx k_BTt/(N\zeta)$.

Since the physical relevance of the imposition of an area constraint is not so much in the particular value of the area but in its conservation, we believe the present approach to describe the dynamics of a Gaussian and (approximate) self-avoiding ring captures the essential physics of the problem. The present description will, however, benefit from computer simulation studies where the effects due to excluded volume interactions can be included in a more rigorous way.

IV. CONCLUSIONS

In summary, the present theory illustrates the effects of a relatively simple global constraint on the stochastic dynamics of noninteracting polymer chains. We show that the presence of the area constraint couples the dynamics of the Cartesian components of the spatial vector $\mathbf{r}(s,t) = [r_x(s,t), r_y(s,t)]$ through the time dependent Lagrange multiplier. The time dependence of the Lagrange multiplier can be determined as a dynamical response to the initial perturbation of area modes such that the condition $dA(t)/dt=0$ is satisfied at all times. At very short times, that is $t \ll \tau$, the Lagrange multiplier decays slowly with an inverse dependence on time, where $\tau = N^2 b^2 \zeta / 8\pi^2 k_B T$. For long times, that is $t \gg \tau$, the Lagrange multiplier is mainly determined by the inverse of the first mode of the area, which on an average is a random walk about a circle. As opposed to the relaxation of the internal modes of a ring without constraint, the area constraint changes the nature of relaxation of these modes dramatically. At long times the dynamics is completely determined by the first (Rouse) mode which does not relax. The first mode is associated with the rotation of the ring; the mean-square displacement of the radius at long times is found to be diffusive. The effects due to self-avoidance, when included in an effective way, lead to the similar predictions with different relaxation time scales.

Some of the (local) problems associated with the complex loops (see Fig. 1) formed by ideal Gaussian chains can be taken care of by accounting for semiflexibility. In a future publication we are going to extend the present formalism to study the static and dynamical properties of semiflexible loops constrained to enclose a constant area [16].

Although the idea was to present a general theory for the dynamics of area preserving systems, the present approach can serve as a simple description to understand some of the dynamical aspects of polymer systems under topological constraints, entanglements and two-dimensional vesicles—systems where the area conservation must be explicitly accounted.

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