

Polymer dynamics in time-dependent Matheron–de Marsily flows: An exactly solvable model

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We introduce a model of random layered media, extending the Matheron–de Marsily model: Here we allow for the flows to change in time. For such layered structures, we solve exactly the equations of motion for single particles and also for polymers modelled as Rouse chains. The results show a rich variety of dynamical patterns.

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I. INTRODUCTION

The dynamics of particles and particle assemblies in random force fields is a subject of intense current interest (see Refs. [1–3] and references therein). Such fields often lead to qualitative deviations from simple dynamic patterns, and result in the anomalous diffusion of the particles involved. A standard prototype model is that of Matheron and de Marsily flows (Mdm) [1–10], originally designed to describe the transport of a solute in porous media. Similar mathematical forms arise when treating electrons in random potentials or spin depolarization in random fields [10]. In the Mdm model the environment is viewed as consisting of layers of force fields [4]. The particle mean-square displacement (MSD) in the direction parallel to the flows, say, along the Y axis, $\langle Y^2(t) \rangle$, can be evaluated exactly; it has been shown that it grows as $\langle Y^2(t) \rangle \sim t^{3/2}$ [4,5,8], t being the time. Recently the dynamics of Rouse polymer chains in time-independent Mdm flows was also discussed and several exact results have been derived [1,2]. In particular, it has been shown that the MSD of some tagged bead of the chain may display different dynamical regimes depending on whether the time of observation is shorter or longer than the so-called Rouse time t_R . Now t_R goes as N^2 , where N is the degree of polymerization, i.e., the chain's length [11–13]. For times shorter than t_R a subballistic law $\langle Y^2(t) \rangle \sim t^{7/4}$ was derived, while it was shown that for times longer than t_R the $t^{3/2}$ dependence is restored, the prefactor being a growing function of N . Thus a tagged monomer of a polymer immersed in Mdm flows moves in general faster than an individual particle (i.e., a chain with $N=1$), a fact which has its physical explanation [1,2].

These results concern, however, velocity fields whose directions and magnitudes are random in space but fixed in time: we speak of quenched disorder. For random divergenceless velocity flows, for which the flows change with time, we show in the following that new results emerge.

In the present paper we present exact dynamical solutions both for individual particles and for long Rouse chains moving in time-dependent, random layered media. Distinct from previous works [1,2,4,5,8], we now allow the velocities in the layers to change randomly with time. We thus take into account the fact that the environment itself may be subject to dynamical processes, thereby introducing new time scales

into the problem. By this the time fluctuations of the flow give rise to interesting dynamical behaviors. In particular, we show that at intermediate times ($t \ll t_R$) the MSD of any tagged bead of a polymer chain follows $\langle Y^2(t) \rangle \sim t^{3/4}$, i.e., the MSD moves faster than the Rouse law $\langle Y^2(t) \rangle \sim t^{1/2}$ which holds in the flow-free case [12,13]. On the other hand, at times $t \gg t_R$, we recover a diffusive behavior, in which, however, the effective diffusion constant scales as $N^{-1/2}$ for sufficiently long chains, i.e., vanishes with N at a slower rate than the Rouse diffusion constant, which goes as $1/N$.

The paper is structured as follows: In Sec. II we formulate the model and introduce the basic notation. In Sec. III we analyze the dynamics of an individual particle subject to time-dependent Mdm flows. Section IV is devoted to the analysis of the dynamics of a tagged bead of an infinitely long Rouse chain, while Sec. V deals with effects typical for finite chains. We conclude with a discussion and a brief summary of results in Sec. VI.

II. THE MODEL

A standard polymer model due to Rouse [11] consists in viewing the macromolecule as a series of N beads, linearly connected by harmonic springs. Its dynamics in solution, but subject to external force fields and excluding hydrodynamic interactions and steric hindrances, is given by the Langevin equation [11–13]

$$\zeta \frac{d\mathbf{R}_n}{dt} = K(\mathbf{R}_{n+1} + \mathbf{R}_{n-1} - 2\mathbf{R}_n) + \mathbf{F}(\mathbf{R}_n, t) + \boldsymbol{\eta}(n, t), \quad (1)$$

for $1 \leq n \leq N$, complemented by $\mathbf{R}_0 \equiv \mathbf{R}_1$ and $\mathbf{R}_N \equiv \mathbf{R}_{N+1}$. In this equation ζ is the coefficient of friction, \mathbf{R}_n is the position of the n th monomer, $K = 3k_B T/b^2$ is the spring constant accounting for the Hookean interaction of the monomers, $k_B T$ being the temperature multiplied by the Boltzmann constant and b the average distance between the beads, and $\boldsymbol{\eta}(n, t)$ represents the thermal noise due to interactions with the solvent. In Eq. (1) the $\mathbf{F}(\mathbf{R}_n, t)$ denote the extra forces due to the imposed velocity fields. Equation (1) is a simplified description of the dynamics of a polymer in θ solutions [12,13].

Treating the index n as continuous leads to the replacement of the discrete term $(\mathbf{R}_{n+1} + \mathbf{R}_{n-1} - 2\mathbf{R}_n)$ by the La-

placian operator $\partial^2 \mathbf{R}_n / \partial n^2$ and of $\mathbf{R}_0 \equiv \mathbf{R}_1$ and $\mathbf{R}_N \equiv \mathbf{R}_{N+1}$ by the Rouse boundary conditions [12]

$$\frac{\partial \mathbf{R}_n}{\partial n} = 0, \text{ for } n=0 \text{ and } n=N. \quad (2)$$

Next, we specify the forces entering the right-hand side (RHS) of Eq. (1). We let, as usual, the thermal noise be Gaussian with zero mean; due to the fluctuation-dissipation theorem, the second moment takes the form

$$\overline{\eta_\alpha(n, t) \eta_\beta(n', t')} = 2k_B T \zeta \delta_{\alpha, \beta} \delta_{n, n'} \delta(t - t'). \quad (3)$$

In Eq. (3) we let the Greek indices denote the Cartesian components. The MdM model is obtained by assuming layered flows, say, by taking the forces to be along the Y axis, but to depend solely on the X component (see, e.g., Fig. 1 in [1]):

$$\mathbf{F}(\mathbf{R}_n, t) = (0, f(X_n, t), 0). \quad (4)$$

This choice of \mathbf{F} models a layered medium along the X axis; each layer has a random (but for all points of the layer fixed) velocity pointing along the Y axis. Due to the uncoupling of the different components in the Rouse model, the dynamics in the transversal plane (i.e., the X and Z components) is not influenced by the presence of the velocity fields. However, as we shall see, the motion parallel to the Y axis is dramatically changed.

The random force $\mathbf{F}(\mathbf{R}_n, t)$ (i.e., its Y component) is assumed to be Gaussian and zero centered. For the second moment we take

$$\langle f(X, t) f(X', t') \rangle = \frac{\Delta}{2\Gamma} \delta(X - X') e^{-|t - t'|/\Gamma}. \quad (5)$$

Note that the strength of the random velocity field depends on the constants Γ and Δ . Equation (5) defines a changing environment with a short-term memory, exponentially decreasing on the time scale Γ ; we will call Γ the renewal time. In the limit $\Gamma \rightarrow \infty$ and keeping the ratio Δ/Γ fixed we recover the standard quenched MdM model. We shall denote this limiting procedure as the *quenched limit* in the rest of the paper. On the other hand, when $\Gamma \rightarrow 0$, $\exp(-|t|/\Gamma)/(2\Gamma)$ tends to the Dirac $\delta(t)$ distribution; this limit allows us to study an environment without memory. We distinguish averages over thermal histories from averages over configurations of the velocity field by using an overbar for the former and angular brackets for the latter.

III. DYNAMICS OF A SINGLE PARTICLE

To fix the ideas, we start with the case of a single bead in time-dependent MdM flows. Then $N=1$ and $K=0$. Because of the decoupling of the different coordinates, the X and Z components of the particle displacement obey the force-free Langevin equation

$$\zeta \frac{dX}{dt} = \eta_x(t), \quad (6)$$

with $\eta_x(t)$ being the X component of the thermal noise. Equation (6) yields for the MSD averaged over thermal histories the usual diffusion result

$$\overline{X^2(t)} = 2 \frac{k_B T}{\zeta} t = 2Dt. \quad (7)$$

Through the last relation we have introduced the “bare” diffusion constant D . For the Y component we have to solve the equation

$$\zeta \frac{dY}{dt} = \eta_y(t) + f(X(t), t), \quad (8)$$

with $f(X(t), t)$ being the random function of Eq. (5). The solution of Eq. (8) is

$$Y(t) = \frac{1}{\zeta} \int_0^t d\tau [\eta_y(\tau) + f(X(\tau), \tau)], \quad (9)$$

where we set $Y(0)=0$. Being interested in the mean-square displacement we have

$$\langle \overline{Y^2(t)} \rangle = 2Dt + \frac{1}{\zeta^2} \int_0^t dt_1 \int_0^t dt_2 \langle \overline{f(X(t_1), t_1) f(X(t_2), t_2)} \rangle, \quad (10)$$

by noting that the different sources of randomness are decoupled. Then, by virtue of Eq. (5) we have for the second term

$$\begin{aligned} \int_0^t dt_1 \int_0^t dt_2 \langle \overline{f(X(t_1), t_1) f(X(t_2), t_2)} \rangle \\ = \frac{\Delta}{2\Gamma} \int_0^t dt_1 \int_0^t dt_2 \overline{\delta(X(t_1) - X(t_2))} e^{-|t_1 - t_2|/\Gamma}. \end{aligned} \quad (11)$$

Now it is a simple matter to average the δ function on the RHS of Eq. (11), by making use of its Fourier representation; this yields

$$\begin{aligned} \overline{\delta(X(t_1) - X(t_2))} &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \overline{\exp\{-ik[X(t_1) - X(t_2)]\}} \\ &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp(-Dk^2|t_1 - t_2|) \\ &= \frac{1}{\sqrt{4\pi D|t_1 - t_2|}}. \end{aligned} \quad (12)$$

Here we noted that the process $X(t)$ is Gaussian and we used in the second line the well-known rule for averaging Gaussian exponential forms. Inserting Eq. (12) into Eq. (11) and integrating leads to

$$\begin{aligned} \langle \overline{Y^2(t)} \rangle &= 2Dt + \frac{\Delta}{2\zeta^2} \sqrt{\frac{\Gamma}{D}} \{ (t/\Gamma - 1/2) \text{erf}[\sqrt{t/\Gamma}] \\ &\quad + \sqrt{t/(\pi\Gamma)} e^{-t/\Gamma} \}, \end{aligned} \quad (13)$$

where $\text{erf}[x]$ denotes the error function, Eq. (7.1.1) in Ref. [14]. Equation (13) is exact and is the main result of this section. From Eq. (13) we have in the limit $t \ll \Gamma$

$$\langle \overline{Y^2(t)} \rangle = 2Dt + \frac{2\Delta\Gamma^{1/2}}{3\zeta^2\sqrt{D\pi}} \left(\frac{t}{\Gamma} \right)^{3/2} + \mathcal{O}\left(\left(\frac{t}{\Gamma} \right)^{5/2} \right), \quad (14)$$

where the second term represents the result for standard, quenched MDM flows [4]. The physics underlying such a behavior is well understood [1,2,4,6,7,9] and it is due to dynamically induced correlations in the velocities felt by the particle.

In the opposite limit, $t \gg \Gamma$, we are led to

$$\langle \overline{Y^2(t)} \rangle = 2Dt + \frac{\Delta}{2\zeta^2\Gamma} \sqrt{\frac{\Gamma}{D}} t + \mathcal{O}(1) = 2D_{eff}t + \mathcal{O}(1), \quad (15)$$

where

$$D_{eff} = D + \frac{\Delta}{4\zeta^2\Gamma} \sqrt{\frac{\Gamma}{D}}; \quad (16)$$

i.e., we find diffusion with a renormalized diffusion coefficient.

Thus for large times t the fluctuations of the environment (flow) contribute additively to the diffusion coefficient. Note, however, that now diffusion is anisotropic: Parallel to and perpendicular to the layers one has $D_{||} = D_{eff}$ and $D_{\perp} = D$, respectively. The dependence of D_{eff} on both D and Γ is easily visualized: For larger D the perpendicular motion is more rapid and hence the velocity field viewed by the particle changes more rapidly (and is less efficient); furthermore, a decrease in Γ leads to a similar effect. On the other hand, in the $\Gamma \rightarrow \infty$ limit (with Δ/Γ fixed) D_{eff} diverges, a sign that the motion gets to be superdiffusive; see Eq. (14).

Since the disorder changes completely on the time scale Γ , one may view Eq. (15) as arising from renewals of the process in Eq. (14) (with total loss of memory) every τ units of time, where τ is of the order of Γ . In fact, since the crossover in behavior from $[2\Delta\Gamma^{1/2}/3\zeta^2(\pi D)^{1/2}](t/\Gamma)^{3/2}$ to $[\Delta/2\zeta^2(\Gamma D)^{1/2}]t$ occurs at $t_c = 9\pi\Gamma/16 \approx 1.767\Gamma$, we reproduce Eq. (16) exactly if we take $\tau = t_c$.

IV. INFINITELY LONG ROUSE CHAIN

We consider next the opposite case of an infinitely long Rouse chain. For a given thermal history, the solution of Eq. (1) for the Y component of the displacement of the n th bead can be readily found by standard means (see Refs. [1,2]) and reads

$$Y_n(t) = \frac{1}{\zeta} \int_0^t d\tau \int_{-\infty}^{\infty} dl P(n-l, t-\tau) [f(X_l(\tau), \tau) + \eta_y(l, \tau)], \quad (17)$$

where we again, for simplicity, assumed that $Y_n(0) = 0$. Here $P(l, \tau)$ is the Green's function solution of the one-dimensional (1D) diffusion equation

$$P(l, \tau) = \sqrt{\frac{\zeta}{4\pi K\tau}} \exp\left[-\frac{\zeta l^2}{4K\tau}\right]. \quad (18)$$

The MSD of the n th bead, averaged both over thermal histories and over random velocity fields, takes the form

$$\begin{aligned} \langle \overline{Y_n^2(t)} \rangle &= 2D \left(\frac{\zeta}{2\pi K} \right)^{1/2} t^{1/2} + \frac{\Delta}{2\Gamma\zeta^2} \int_0^t d\tau_1 \int_0^t d\tau_2 \int_{-\infty}^{\infty} dl_1 \\ &\times \int_{-\infty}^{\infty} dl_2 P(n-l_1, t-\tau_1) P(n-l_2, t-\tau_2) \\ &\times e^{-|\tau_1 - \tau_2|/\Gamma} \overline{\delta(X_{l_1}(\tau_1) - X_{l_2}(\tau_2))}, \end{aligned} \quad (19)$$

where we used the second moment of the velocity field, given by Eq. (5).

To proceed further, we need to know $\overline{\delta(X_{l_1}(\tau_1) - X_{l_2}(\tau_2))}$. This form can be evaluated exactly (see Refs. [1,2,12,13] for more details). The result (for $\tau_1 \leq \tau_2$) is explicitly

$$\overline{\delta(X_{l_1}(\tau_1) - X_{l_2}(\tau_2))} = \left(\frac{K}{4\pi\zeta D^2} \right)^{1/4} M(l_2 - l_1, \tau_1, \tau_2)^{-1/2}, \quad (20)$$

in which the function $M(l, \tau_1, \tau_2)$ stands for

$$\begin{aligned} M(l, \tau_1, \tau_2) &= (2\tau_1)^{1/2} + (2\tau_2)^{1/2} \\ &- 4 \left(\frac{\pi K}{\zeta} \right)^{1/2} \int_0^{\tau_1} d\tau P(l, \tau_1 + \tau_2 - 2\tau). \end{aligned} \quad (21)$$

Inserting Eqs. (20) and (21) into Eq. (19) and reverting to dimensionless variables, say, by setting

$$\theta_1 = \tau_1/t, \quad \theta_2 = \tau_2/t, \quad \theta = \tau/t,$$

$$z_1 = (l_1 - n) \left(\frac{\zeta}{4Kt} \right)^{1/2}, \quad z_2 = (l_2 - n) \left(\frac{\zeta}{4Kt} \right)^{1/2}, \quad (22)$$

we finally arrive at the expression

$$\langle \overline{Y_n^2(t)} \rangle = 2D \left(\frac{\zeta}{2\pi K} \right)^{1/2} t^{1/2} + \frac{\Delta}{\pi\Gamma\zeta^2} \left(\frac{K}{4D^2\pi\zeta} \right)^{1/4} t^{7/4} g(t/\Gamma), \quad (23)$$

with $g(\eta)$ being the dimensionless function:

$$\begin{aligned} g(\eta) &= \int_0^1 d\theta_2 \int_0^{\theta_2} d\theta_1 e^{-(\theta_1 - \theta_2)\eta} \int_{-\infty}^{\infty} dz_1 \\ &\times \int_{-\infty}^{\infty} dz_2 \frac{e^{-z_1^2/(1-\theta_1) - z_2^2/(1-\theta_2)}}{\sqrt{(1-\theta_1)(1-\theta_2)} \tilde{M}(z_1 - z_2, \theta_1, \theta_2)}, \end{aligned} \quad (24)$$

where for $\theta_2 \geq \theta_1$ the function $\tilde{M}(z, \theta_1, \theta_2)$ is

$$\tilde{M}(z, \theta_1, \theta_2) = \sqrt{2\theta_1} + \sqrt{2\theta_2} - 2 \int_0^{\theta_1} d\theta \frac{e^{-z^2/(\theta_1 + \theta_2 - 2\theta)}}{\sqrt{\theta_1 + \theta_2 - 2\theta}}. \quad (25)$$

In the limit $\Gamma \rightarrow \infty$ (quenched MdM flows) $\eta = t/\Gamma$ tends to zero and $g(\eta)$ to a constant. Hence, for $\Gamma \rightarrow \infty$ and not-too-small t one has $\langle Y_n^2 \rangle \sim t^{7/4}$; this reproduces precisely the corresponding result derived in Refs. [1] and [2]. Moreover, we expect this dynamical behavior to show up also for finite Γ , as long as $t \ll \Gamma$, i.e. $\eta \ll 1$.

Turning now to finite but small Γ , for $t \gg \Gamma$, i.e., $\eta = t/\Gamma \gg 1$, the leading large- η behavior of $g(\eta)$ can be found by integrating in Eq. (24) over θ_1 by parts with respect to $\exp(\theta_1 \eta)$. We find that $g(\eta)$ has the form

$$g(\eta) = \frac{C}{\eta} + \mathcal{O}\left(\frac{1}{\eta^2}\right), \quad (26)$$

where C is a dimensionless constant, given by

$$C = \int_0^1 d\theta \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \frac{e^{-(z_1^2 + z_2^2)/(1-\theta)}}{(1-\theta) \sqrt{\tilde{M}(z_1 - z_2, \theta, \theta)}}. \quad (27)$$

Inserting now Eq. (26) into Eq. (23) we find that the MSD of any bead of an infinitely long Rouse chain obeys

$$\begin{aligned} \langle \overline{Y_n^2(t)} \rangle &= 2D \left(\frac{\zeta}{2\pi K} \right)^{1/2} t^{1/2} + \frac{C\Delta}{\pi\zeta^2} \left(\frac{K}{4D^2\pi\zeta} \right)^{1/4} t^{3/4} \\ &+ \mathcal{O}(t^{-1/4}). \end{aligned} \quad (28)$$

The significant terms of Eq. (28) can be understood as follows: The first term is just the Rouse result in the absence of flows. The second term arises due to the time dynamics of the MdM flows, to be contrasted with the $t^{7/4}$ term for quenched MdM flows. This term appears, of course, even when the time correlation in Eq. (5) is of δ form, i.e., for $\Gamma \rightarrow 0$.

Therefore, we have for monomers attached to long polymer chains that at long times $\langle Y_n^2(t) \rangle \sim t^{3/4}$, i.e., that the exponent of the anomalous diffusion is larger than in the force-free case. One may contrast this behavior to that of a single particle, where at long times time-dependent velocity fields only change the diffusion constant, but leave the exponent of t (unity) unchanged. Hence the influence of the velocity fields on the monomer's motion differs from that of the thermal noise. The difference can be traced to the form of the disorder; the solvent's role is included through MdM $\delta(X_{l_1}(t_1) - X_{l_2}(t_2))$ fields, which depend on the X components of the positions of the beads, while thermal noise depends on δ_{l_1, l_2} . This means that while different monomers always experience different forces from the heat bath, distinct monomers with the same X components (there are many such monomers, since the polymer's projection on the X axis corresponds to a simple random walk) experience identical velocity fields, a fact which qualitatively enlarges $\langle Y_n^2(t) \rangle$.

V. FINITE ROUSE CHAINS

For finite Rouse chains there appears yet another time scale, namely, the so-called Rouse time $t_R = \zeta N^2/(\pi^2 K)$ [11–13], t_R being the largest internal relaxation time of the structure. To display its role we start by solving Eq. (1) for finite N . The solution is found most readily in terms of normal coordinates [12], introduced, say, for $Y_n(t)$, through

$$Y_n(t) = \sum_{p=-\infty}^{\infty} \cos(p\pi n/N) Y(p, t), \quad (29)$$

and similarly for $X_n(t)$ and $Z_n(t)$. Inserting these forms into the equation of motion, Eq. (1), and solving yields straightforwardly for the X component [1]

$$X(p, t) = \frac{1}{N\zeta} \int_0^t d\tau \int_0^N dn \, \eta_x(n, \tau) \cos(p\pi n/N) e^{-p^2(t-\tau)/t_R}, \quad (30)$$

and similarly for the Z component. For the Y component one has instead

$$\begin{aligned} Y(p, t) &= \frac{1}{N\zeta} \int_0^t d\tau \int_0^N dn \, [\eta_x(n, \tau) + f(X_n(\tau), \tau)] \\ &\times \cos(p\pi n/N) e^{-p^2(t-\tau)/t_R}. \end{aligned} \quad (31)$$

The behavior of the beads depends on the ratio t/t_R . For short times $t \ll t_R$ the sums over p for $X_n(t)$, $Y_n(t)$, and $Z_n(t)$, e.g., Eq. (29), can be converted into integrals; exemplarily, inserting Eq. (31) into Eq. (29) and performing the integration leads to Eq. (17). Thus for $t \ll t_R$ each bead behaves as if it were part of an infinite chain: Hence the results from the previous section apply. In the opposite regime, for $t \gg t_R$, only the zeroth mode $p=0$ contributes significantly to Eq. (31), and the motion of each bead follows closely that of the center of mass (c.m.) of the chain. In the case of the X and Z components, this is a diffusive behavior with the renormalized diffusion constant $D \rightarrow D/N$ [11–13]. For the Y component, however, we have for $t \gg t_R$ approximately

$$\begin{aligned} \langle \overline{Y_n^2(t)} \rangle &\approx \langle \overline{Y^2(0, t)} \rangle = 2 \frac{D}{N} t + \frac{\Delta}{2N^2\Gamma\zeta^2} \int_0^t d\tau_1 \int_0^t d\tau_2 \int_0^N dn_1 \\ &\times \int_0^N dn_2 \, \overline{\delta(X_{n_1}(\tau_1) - X_{n_2}(\tau_2))} e^{-|\tau_1 - \tau_2|/\Gamma}. \end{aligned} \quad (32)$$

We remark that the terms on the RHS of Eq. (32) describe the dynamics of the Y component of the chain c.m. for all t . The evaluation of Eq. (32) is rendered complex for finite N due to the appearance of the two-time δ function in the integral. It is, however, possible to proceed along the lines of Ref. [2], but this is outside the scope of the present article. Since the analysis simplifies for $\Gamma \rightarrow \infty$ and for $\Gamma \rightarrow 0$, we shall consider only these two cases in the following.

For $\Gamma \rightarrow \infty$ the flows get to be time independent; then the approach follows the derivation given in [1,2] for quenched

MdM flows. There it was found that the leading behavior of the bead's motion obeys [Eq. (36a) of Ref. [1], here in our notation]

$$\langle \overline{Y_n^2(t)} \rangle \sim \frac{\Delta}{\Gamma \zeta^2} \sqrt{\frac{N}{D}} t^{3/2}; \quad (33)$$

that is, the c.m. moves practically as an individual particle, i.e., Eq. (14), with D being, however, replaced by D/N .

For $\Gamma \rightarrow 0$, we have for the second term (call it I) in Eq. (32)

$$I = \frac{\Delta}{N^2 \zeta^2} \int_0^t d\tau \int_0^N dn_1 \int_0^N dn_2 \overline{\delta(X_{n_1}(\tau) - X_{n_2}(\tau))}. \quad (34)$$

For $t \gg t_R$ most of the τ in Eq. (34) also obey $\tau \gg t_R$, so that we may view the Gaussian X process as stationary, i.e., $\overline{(X_{n_1}(\tau) - X_{n_2}(\tau))^2} = D\zeta|n_1 - n_2|/K$, independent of τ . Hence

$$\begin{aligned} \overline{\delta(X_{n_1}(\tau) - X_{n_2}(\tau))} &= \int_0^\infty \frac{dk}{2\pi} \overline{e^{ik[X_{n_1}(\tau) - X_{n_2}(\tau)]}} \\ &= \int_0^\infty \frac{dk}{2\pi} e^{-k^2 D\zeta|n_1 - n_2|/2K} \\ &= \sqrt{\frac{K}{2D\pi\zeta|n_1 - n_2|}}. \end{aligned} \quad (35)$$

Inserting now Eq. (35) into Eq. (34) and performing the integrations leads to

$$\begin{aligned} I &= \frac{\Delta}{N^2 \zeta^2} \sqrt{\frac{K}{2D\pi\zeta}} \int_0^t d\tau \int_0^N dn_1 \int_0^N dn_2 |n_1 - n_2|^{-1/2} \\ &= \frac{8\Delta}{3\zeta^2} \sqrt{\frac{K}{2D\pi\zeta}} \frac{t}{\sqrt{N}}. \end{aligned} \quad (36)$$

Using this expression in Eq. (32) we see that $\langle \overline{Y_n^2(t)} \rangle = D_{eff}^N t$, where now D_{eff}^N is

$$D_{eff}^N = \frac{D}{N} + \frac{4\Delta}{3\zeta^2} \sqrt{\frac{K}{2D\pi\zeta}} \frac{1}{\sqrt{N}}. \quad (37)$$

Again the time-dependent MdM flows are seen to produce a ‘‘correction’’ to the diffusion constant at long times; this correction is of more importance the longer the chains. For infinite chains D_{eff}^N vanishes, a sign of the appearance for $N \rightarrow \infty$ of the sublinear, $t^{3/4}$ behavior of Eq. (28). The result can be understood in terms of the renewal of the process of Eq. (28): Thus for $t \gg t_R \gg \Gamma$, assuming a loss of memory after each t_R units of time, $\langle \overline{Y_N^2(t)} \rangle$ can be expressed as being around t/t_R times $(C\Delta/(\pi\zeta^2))[K/(4D^2\pi\zeta)]^{1/4} t_R^{3/4}$. This leads to a correction of the diffusion constant of

$$\frac{1}{2t_R} \frac{C\Delta}{\pi\zeta^2} \left(\frac{K}{4D^2\pi\zeta} \right)^{1/4} t_R^{3/4} = \frac{3C}{8\pi^{1/4}} \frac{4\Delta}{3\zeta^2} \sqrt{\frac{K}{2D\pi\zeta}} \frac{1}{\sqrt{N}}, \quad (38)$$

which is $3C/(8\pi^{1/4})$ times the correction in Eq. (37).

A similar argument can be put forth when $t \gg \Gamma \gg t_R$. In this case, $\langle \overline{Y_n^2(t)} \rangle$ can be viewed as arising from renewals (every Γ units of time) of the process given by Eq. (33). This leads to yet another effective diffusion constant \tilde{D}_{eff}^N , which besides D/N has an additional term proportional to

$$\frac{\Delta}{\zeta^2} \sqrt{\frac{N}{D\Gamma}}. \quad (39)$$

This reproduces (after replacing D/N by D) the result of the single-particle case, Eq. (16).

We summarize the findings for the MSD of a bead on the finite Rouse chain. When $t \gg \max(t_R, \Gamma)$, there is normal but anisotropic diffusion of the bead under observation, described by the diffusion constant $D_\perp = D$ in the directions perpendicular to the flow and an effective diffusion constant $D_\parallel > D$ parallel to the flow. The value of D_\parallel depends on whether $t_R \ll \Gamma$ or $t_R \gg \Gamma$: For $t_R \ll \Gamma$, $D_\parallel = \tilde{D}_{eff}^N$ [see Eq. (39)], and for $t_R \gg \Gamma$, $D_\parallel = D_{eff}^N$, Eq. (37). In the short-time regime $t \ll \min(t_R, \Gamma)$, we always have $Y_n^2(t) \sim t^{7/4}$. However, the intermediate regime again depends on the magnitudes of t_R and Γ . If $t_R \ll \Gamma$ we observe $\langle \overline{Y_n^2(t)} \rangle \sim t^{3/2}$ [Eq. (33)] in the regime $t_R \ll t \ll \Gamma$. But if, on the other hand, $\Gamma \ll t_R$, then for times t obeying $\Gamma \ll t \ll t_R$, the MSD behaves as $\langle \overline{Y_n^2(t)} \rangle \sim t^{3/4}$. Our model gives therefore rise to a very rich dynamical behavior.

VI. CONCLUSION

In this work we introduced a new variant of the Matheron–de Marsily model of layered random media, in which the velocity field is also allowed to change with time. We solved exactly the equations describing the dynamics of a single particle and of beads belonging to infinite Rouse chains in time-dependent MdM flows. For short times and slowly changing media, we recovered the results of the standard quenched MdM model. For large times we found normal diffusion in the cases of a single particle and of a finite Rouse chain, and we computed the corrections to the diffusion constant. For the infinite Rouse chain we found a surprisingly fast increase with time of the mean-square displacement, a result also valid for finite Rouse chains in intermediate-time regimes.

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