

Diffusion in a fluctuating random geometry

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A theoretical analysis is presented of the self-diffusion of a particle in a disordered and fluctuating one-dimensional geometry. A general result is obtained, showing how geometrical fluctuations enhance the rate of diffusion measured in a laboratory-fixed frame. This result is relevant for understanding molecular transport in certain complex fluids and biological systems. Explicit results are given for three different dynamic models, illustrating how diffusion measurements can be used to extract information about the orientational distribution and dynamics of segments of polymers or wormlike micelles in isotropic solutions and liquid-crystalline phases. [S1063-651X(97)06401-5]

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I. INTRODUCTION

Diffusion in disordered media has received considerable attention in recent years, mainly with a view to applications in solid-state physics [1–3]. Much of this work focuses on diffusion with random transition rates and on anomalous diffusion on percolation clusters and fractals. In the present work, we address a particular case of spatial disorder, namely, diffusion in a random geometry. Despite its fundamental nature and potential applications, this problem has remained virtually unexplored.

The motivation for our interest in the problem is as follows. In complex fluids, such as self-assembled amphiphile-based systems of biological or synthetic origin, small molecular species can diffuse freely over interfaces or within structures whose geometry fluctuates in space and time due to thermal motion. A macroscopic self-diffusion experiment, e.g., using pulsed-gradient spin-echo NMR [4] or fluorescence recovery after photobleaching [5], essentially measures the mean-square displacement $\langle x^2(t) \rangle$, along a laboratory-fixed axis (x), or the corresponding long-time diffusion coefficient

$$D_x = \lim_{t \rightarrow \infty} \langle x^2(t) \rangle / 2t. \quad (1.1)$$

Our objective is to relate the measured laboratory-frame diffusion coefficient D_x to the curvilinear diffusion coefficient D_s describing the diffusional motion of the mobile species in the curvilinear space defined by the microstructure of the complex fluid. In general, the local orientation of the microstructure fluctuates in time. The measured D_x then reflects the equilibrium orientational statistics of the microstructure as well as its reorientational dynamics and hence can provide information about both these aspects of the system. In addition, the relation between D_x and D_s is of interest in the study of material transport and chemical kinetics in complex fluids and biological environments.

In the present work, we study a random curvilinear geometry in one dimension, allowing exact analytical results to be obtained. Real systems for which these results should be applicable include diffusion of amphiphiles or solubilized hydrophobic species in isotropic and nematic phases of very

long wormlike micelles and in hexagonal liquid crystals, diffusion of water or ions through the aqueous channels in reversed hexagonal liquid crystals, and in certain microemulsions, diffusion of an absorbed species along a polymer chain in isotropic or nematic phases and along extended supramolecular biostructures.

We begin, in Sec. II, by treating the case of a static curvilinear geometry (quenched disorder), focusing on the role of spatial orientational correlations. Certain limiting forms of the general result of Sec. II are then shown to reduce to various known results for a random walk on a random walk [6], the stochastic Lorentz model [7], and the polymer reptation model [8,9].

In Sec. III, we address the more general case of diffusion in a fluctuating curvilinear geometry. While a continuum description was used in Sec. II, the general case of Sec. III is more conveniently treated in terms of a discrete random-walk model. The problem of obtaining the macroscopic diffusion coefficient D_x is then equivalent to calculating the asymptotic mean-square displacement for a one-dimensional symmetric random walk with a step length that fluctuates in time and space.

The general result for D_x derived in Sec. III is applied in Sec. IV to several models for the reorientational dynamics of the curvilinear geometry, including the Rouse model of polymer dynamics [9,10] and the viscoelastic continuum model of nematic director fluctuations [11,12]. We conclude, in Sec. V, with some remarks on possible applications and extensions of the present theoretical results.

II. STATIC GEOMETRY

Consider a molecular species (referred to as the ‘‘particle’’) that diffuses freely along an unbounded, continuous space curve (referred to as the ‘‘chain’’). The geometry (or configuration) of a static chain defined by the parametric equation $\mathbf{r}=\mathbf{r}(s)$ can be specified by giving the orientation of the unit tangent vector $\mathbf{u}(s)=d\mathbf{r}/ds$ as a function of the curvilinear coordinate s [13]. As the orientational variable, we choose the projection of $\mathbf{u}(s)$ on the laboratory-fixed x axis (along which the macroscopic diffusion coefficient D_x is measured), i.e., $\zeta(s)=\mathbf{u}(s)\cdot\hat{\mathbf{x}}$. The ζ distribution may be isotropic, as in a solution of long polymers or micelles, or an-

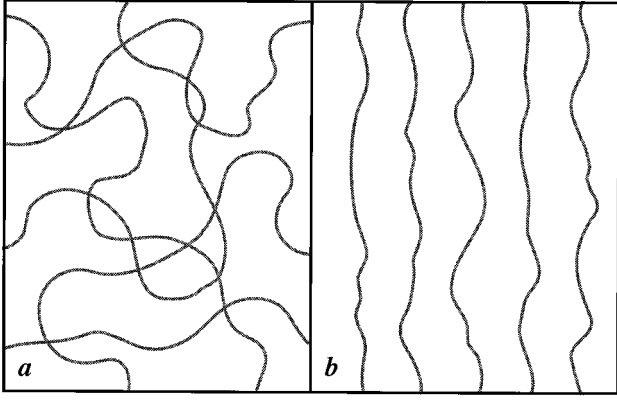


FIG. 1. Schematic illustration of (a) an isotropic and (b) an anisotropic system of polymer chains or wormlike micelles.

isotropic, as in a nematic or hexagonal liquid crystal (cf. Fig. 1). The chain is taken to be homogeneous, i.e., its statistical properties are translationally invariant in the curvilinear space. No other restrictions are imposed on the geometry of the chain, which, in general, is neither planar nor in a one-to-one correspondence with the x axis.

The net displacement $x(s)$ along the x axis corresponding to a given curvilinear displacement s along the chain is [13]

$$x(s) = \int_0^s ds' \zeta(s'), \quad (2.1)$$

so that

$$\langle x^2(s) \rangle = \int_0^s ds' \int_0^s ds'' \langle \zeta(s') \zeta(s'') \rangle, \quad (2.2)$$

where the angular brackets denote a statistical average over an ensemble of chain configurations. This reflects the fact that the mean-square displacement obtained from a macroscopic diffusion measurement is an average over a large number of particles distributed over different chains and with different initial positions on the same chain. The homogeneity of the chain implies that

$$\langle \zeta(s') \zeta(s'') \rangle = \langle \zeta(0) \zeta(s'' - s') \rangle, \quad (2.3)$$

whereby Eq. (2.2) can be transformed into

$$\langle x^2(s) \rangle = \langle \zeta \rangle^2 s^2 + 2 \int_0^s ds' (s - s') g(s'), \quad (2.4)$$

where we have introduced the spatial orientational correlation function

$$g(s) = \langle \zeta(0) \zeta(s) \rangle - \langle \zeta \rangle^2. \quad (2.5)$$

The particle diffuses along the chain with a curvilinear self-diffusion coefficient D_s . Since this diffusion process is independent of the geometry of the chain, the mean-square displacement after a time t can be obtained as

$$\langle x^2(t) \rangle = \int_{-\infty}^{\infty} ds f_s(s, t) \langle x^2(s) \rangle, \quad (2.6)$$

where $f_s(s, t)$ is the usual one-dimensional diffusion propagator

$$f_s(s, t) = (4\pi D_s t)^{-1/2} \exp[-s^2/(4D_s t)]. \quad (2.7)$$

Combining Eqs. (1.1), (2.4), (2.6), and (2.7) and noting that, due to the homogeneity of the chain, the integrand in Eq. (2.6) is an even function of s , we obtain the desired result for the case of a static chain

$$D_x/D_s = \langle \zeta \rangle^2 + \pi^{-1/2} \lim_{t \rightarrow \infty} (D_s t)^{-3/2} \int_0^{\infty} ds \times \exp[-s^2/(4D_s t)] \int_0^s ds' (s - s') g(s'). \quad (2.8)$$

As long as the spatial correlation function $g(s)$ decays with s , as it must in any physical system, the integral over s' in Eq. (2.8) grows more slowly than s^2 , which, in turn, implies that the integral over s grows more slowly than $t^{3/2}$. Consequently, spatial orientational correlations of finite range have no effect on the macroscopic diffusion behavior. For a static chain, we thus have the simple result

$$D_x/D_s = \langle \zeta \rangle^2. \quad (2.9)$$

For a static chain, the normal diffusion coefficient, as defined by Eq. (1.1), thus vanishes in the isotropic limit, where $\langle \zeta \rangle = 0$. In this limit the mean-square displacement $\langle x^2(t) \rangle$ grows asymptotically as $t^{1/2}$, so the projected motion is subdiffusive (cf. below).

Despite its simplicity, Eq. (2.9) is a nontrivial result. The effectively measured diffusion process is asymptotically equivalent to a random walk with random step lengths. Even though *spatial* correlations have no effect on the asymptotic diffusion behavior, *temporal* correlations are essential (cf. Sec. III). This is because a static chain exhibits quenched disorder; a step corresponding to a given ‘‘bond’’ in the chain is always of the same length. In contrast, for a random walk with random step lengths but annealed disorder, the step length is determined *a priori* at the time of each jump. In this case, one has instead of Eq. (2.9) the well-known [14] result $D_x/D_s = \langle \zeta^2 \rangle$ (cf. Sec. III B).

It is of some interest to examine the effect of spatial correlations on the mean-square displacement $\langle x^2(t) \rangle$ at a finite time t . If the chain is locally stiff, the spatial correlation function may be taken as

$$g(s) = [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] \exp(-|s|/\lambda), \quad (2.10)$$

with λ the so-called deflection length [15]. In the isotropic limit, Eq. (2.10) reduces to the orientational correlation function for the wormlike chain model, with λ the persistence length [16]. The combination of Eqs. (2.4), (2.6), (2.7), and (2.10) yields

$$\langle x^2(t) \rangle = 2\langle \zeta \rangle^2 D_s t + 2[\langle \zeta^2 \rangle - \langle \zeta \rangle^2] \lambda \{ (4D_s t/\pi)^{1/2} - \lambda [1 - \exp(D_s t/\lambda^2) \operatorname{erfc}(\sqrt{D_s t}/\lambda)] \}. \quad (2.11)$$

In the special case of an isotropic chain, with $\langle \zeta \rangle = 0$ and $\langle \zeta^2 \rangle = \frac{1}{3}$, the asymptotic form of Eq. (2.11) becomes

$$\lim_{t \rightarrow \infty} \langle x^2(t) \rangle = (4\lambda/3)(D_s t / \pi)^{1/2}, \quad (2.12)$$

which is the well-known result for the mean-square segment displacement for a polymer that reptates in a fixed isotropic tube [8,9].

In the complete absence of spatial orientational correlation along the chain,

$$g(s) = [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] \sigma \delta(s), \quad (2.13)$$

which leads to

$$\langle x^2(t) \rangle = 2 \langle \zeta \rangle^2 D_s t + [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] \sigma (4D_s t / \pi)^{1/2}. \quad (2.14)$$

To compare with previous work, we transform this result from a continuous diffusion model to a discrete random walk model with fixed step length σ . With the correspondence rules

$$t \rightarrow N\tau, \quad D_s \rightarrow \sigma^2/2\tau, \quad (2.15)$$

we obtain in place of Eq. (2.14)

$$\langle x^2(N) \rangle / \sigma^2 = \langle \zeta \rangle^2 N + [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] (2N/\pi)^{1/2}. \quad (2.16)$$

This result has previously been derived for the one-dimensional stochastic Lorentz model [7]. While not contributing to the diffusion coefficient, the second term in Eq. (2.16) gives rise to a long-time (proportional to $t^{-3/2}$) tail in the velocity autocorrelation function for this model, a characteristic feature of quenched disorder [7]. The special case of Eq. (2.16) where ζ can adopt only values $+1$ and -1 (with equal probability) has also been obtained as the asymptotic mean-square displacement for a ‘‘random walk on a random walk’’ [6]. [To obtain the generalization of Eq. (2.16) valid for arbitrarily small N , the discrete version of the Gaussian propagator in Eq. (2.7) must be replaced by the exact binomial distribution.]

III. FLUCTUATING GEOMETRY

A. General result

Consider now the more general case where the local orientation of the chain fluctuates not only in space (along the chain) but also in time (at a given position along the chain). Accordingly, we write for the unit tangent vector $\mathbf{u}(s, t)$. It appears to be simpler, however, to use a discrete random-walk description. (Since we are interested only in asymptotic properties, the choice of description is simply a matter of mathematical convenience.) We thus consider a particle that jumps a distance σ forward or backward along the chain at fixed time intervals τ . The correspondence rules are

$$t \rightarrow N\tau, \quad s \rightarrow \alpha\sigma, \quad D_s \rightarrow \sigma^2/2\tau, \quad (3.1)$$

and Eq. (1.1) is replaced by

$$D_x = \lim_{N \rightarrow \infty} \langle x^2(N) \rangle / 2N\tau. \quad (3.2)$$

The net displacement projected on the x axis after N steps is

$$x(N) = \sigma \sum_{n=1}^N \xi(n), \quad (3.3)$$

where $\xi(n)$ is the projection, in units of σ , of the n th step vector. Note that the sign of $\xi(n)$ depends on the direction of the step along the chain as well as on the orientation of the chain segment relative to the x axis. Obviously, $\langle \xi \rangle = 0$ and $\langle \xi^2 \rangle = \langle \zeta^2 \rangle$.

The combination of Eqs. (3.1)–(3.3) yields

$$D_x / D_s = \langle \zeta^2 \rangle + 2 \lim_{N \rightarrow \infty} \sum_{k=1}^{N-1} (1-k/N) C(k), \quad (3.4)$$

where we have introduced the time correlation function

$$C(k) = \langle \xi(n) \xi(n+k) \rangle \quad (3.5)$$

and made use of the stationarity property that $C(k)$ depends on the time difference k but not on the absolute time n . The normal diffusion law, with $\langle x^2(N) \rangle$ growing asymptotically as N , emerges from the present model if the sum $\sum_1^\infty C(k)$ converges [3], in which case Eq. (3.4) simplifies to

$$D_x / D_s = \langle \zeta^2 \rangle + 2 \sum_{k=1}^{\infty} C(k). \quad (3.6)$$

Since the random-walk statistics on the chain are independent of the configuration and dynamics of the chain, it follows that we can express the time correlation function $C(k)$ as a linear combination of space-time correlation functions $g(\alpha, k)$ of all possible α , where $g(\alpha, k)$ is the time-dependent generalization of (the discrete analog of) the spatial correlation function $g(s)$ in Eq. (2.5), i.e.,

$$g(\alpha, k) = \langle \zeta(0,0) \zeta(\alpha, k) \rangle - \langle \zeta \rangle^2. \quad (3.7)$$

As shown in Sec. II for the case of a static chain, spatial correlations of finite range do not affect the asymptotic mean-square displacement (or D_x). This must clearly be the case also for a fluctuating chain. In the absence of spatial correlations, $g(\alpha, k)$ vanishes unless $\alpha=0$ and, after some reflection, one obtains

$$2 \sum_{k=1}^{\infty} C(k) = -g(0,1) + \sum_{k=1}^{\infty} \frac{(2k)!}{4^k (k!)^2} \times [g(0,2k) - g(0,2k+1)]. \quad (3.8)$$

Introducing the reduced correlation function $\tilde{g}(0, k)$, defined through

$$g(0, k) = g(0,0) \tilde{g}(0, k) = [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] \tilde{g}(0, k), \quad (3.9)$$

we obtain with Eqs. (3.6) and (3.8) the desired general result

$$D_x / D_s = \langle \zeta^2 \rangle - [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] [\tilde{g}(0,1) - \Gamma], \quad (3.10a)$$

with

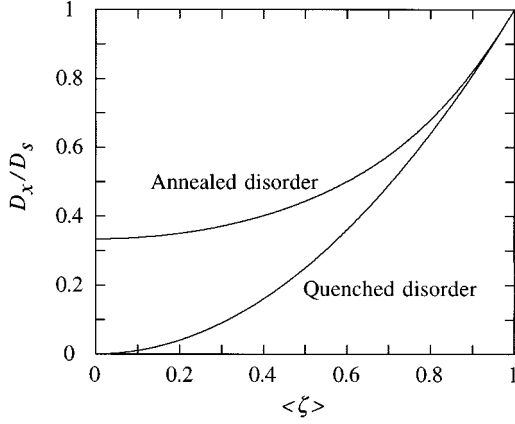


FIG. 2. Bounds on the relative diffusion coefficient D_x/D_s versus the degree of anisotropy $\langle \zeta \rangle$ of the chain. For a given anisotropy, D_x/D_s is bounded from below by $\langle \zeta^2 \rangle$ (quenched disorder) and from above by $\langle \zeta \rangle^2$ (annealed disorder). Except for its limiting values of $\frac{1}{3}$ and 1, the $\langle \zeta^2 \rangle$ curve depends on the shape of the ζ distribution, taken here as $f(\zeta) \propto \exp(\text{const} \times \zeta)$.

$$\Gamma = \sum_{k=1}^{\infty} \frac{(2k)!}{4^k (k!)^2} [\tilde{g}(0, 2k) - \tilde{g}(0, 2k+1)]. \quad (3.10b)$$

By measuring the macroscopic laboratory-frame diffusion coefficient D_x for a molecular species with known curvilinear diffusion coefficient D_s , one can thus obtain information about the orientational distribution of the chain segments as well as about their reorientational dynamics.

B. Limiting cases

The simple results for the two limiting cases of a static chain and a rapidly fluctuating chain (quenched and annealed disorder, respectively) are easily recovered from the general result Eq. (3.10). In the static chain limit, $\tilde{g}(0, k) = 1$ so that $\Gamma = 0$ and Eq. (3.10a) reduces to Eq. (2.9), as required. If chain-segment reorientation is much faster than curvilinear diffusion over the length of the segment, then $\tilde{g}(0, k) = 0$ so that $\Gamma = 0$ again and Eq. (3.10a) reduces to

$$D_x/D_s = \langle \zeta^2 \rangle, \quad (3.11)$$

which is the well-known result for a symmetric random walk with variable step length but with no correlation between the lengths of different steps [14]. Since $\langle \zeta^2 \rangle \geq \langle \zeta \rangle^2$, it follows that chain fluctuations tend to increase the laboratory-frame diffusion coefficient D_x . The two limiting results are plotted in Fig. 2 versus the degree of anisotropy of the chain. For this plot, the relation between $\langle \zeta \rangle$ and $\langle \zeta^2 \rangle$ is fixed by assuming that the aligning potential of mean torque is proportional to $-\zeta$. The difference between the two bounds on D_x is, of course, largest in the isotropic limit, where ζ is uniformly distributed.

In a static chain, the projected step length is always the same for a given chain segment even if there are no correlations between the projected step lengths of different chain segments. Since the diffusing particle returns repeatedly (in fact, infinitely many times) to any chain segment, this induces a temporal correlation that contributes to $C(k)$ at all

times k . Fluctuations in the segment orientation tend to destroy this correlation, thereby increasing the diffusion coefficient D_x .

C. Smoluchowski approach

Further insight into the correlation effect can be obtained by constructing the effective diffusion equation for the projected diffusion process. The curvilinear propagator Eq. (2.7) is the fundamental solution (Green's function) of the usual one-dimensional diffusion equation in the curvilinear coordinate s ,

$$\frac{\partial}{\partial t} f_s(s, t) = D_s \frac{\partial^2}{\partial s^2} f_s(s, t). \quad (3.12)$$

We restrict our attention here to a chain that is sufficiently anisotropic that there is a one-to-one correspondence between s and x . Since $dx = \zeta ds$, it then follows that the effective propagator for the projected diffusion process is given by $f_x(x, t) = f_s(s, t)/\zeta$. Furthermore, since s is a single-valued function of x , we can regard ζ as a function of x and transform Eq. (3.12) into

$$\frac{\partial}{\partial t} f_x(x, t) = \frac{\partial}{\partial x} D(x) \exp[-\phi(x)] \frac{\partial}{\partial x} \exp[\phi(x)] f_x(x, t), \quad (3.13)$$

which is a Smoluchowski equation with the effective nonuniform diffusion coefficient $D(x)$ and the effective potential $\phi(x)$ given by

$$D(x) = D_s \zeta^2, \quad (3.14a)$$

$$\phi(x) = \ln \zeta. \quad (3.14b)$$

In the Smoluchowski picture, the retarding effect of correlations can be viewed as a result of trapping of the particle in potential wells with a small local diffusion coefficient at segments that make a large angle with the x axis (small ζ). It may be noted that the result Eq. (2.9) for the static chain can be derived also from Eq. (3.13) using the mean-first-passage-time method [17] or the equivalent (in one dimension) steady-state flux method [18]. The derivations presented in Secs. II and III are more general, however, since they do not require a one-to-one correspondence between s and x , i.e., they allow the chain to fold back on itself.

IV. DYNAMIC MODELS

To obtain explicit results for the effect of chain dynamics on the diffusion coefficient D_x , the reduced time correlation function $\tilde{g}(0, k)$ entering in Eq. (3.10) must be specified. To this end we shall examine three different dynamic models.

A. Exchange model

In the simplest model, the orientational correlation decays exponentially,

$$\tilde{g}(0, k) = \exp(-k\tau/\tau_c). \quad (4.1)$$

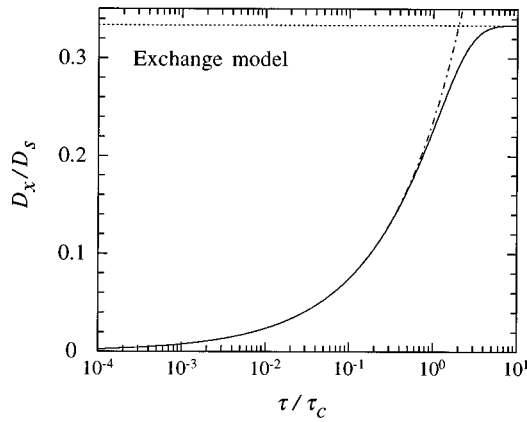


FIG. 3. Variation of the relative diffusion coefficient D_x/D_s for the exchange model, with τ_c the mean residence time of the diffusing particle on a given chain. The solid curve is the exact result Eq. (4.2), while the broken curve is the approximate result Eq. (4.4).

This model might represent exchange of the diffusing molecular species between different chains, with a mean residence time τ_c on a given (static) chain. With Eq. (3.10) we obtain

$$D_x/D_s = \langle \zeta^2 \rangle - [\langle \zeta^2 \rangle - \langle \zeta \rangle^2] [\exp(-\tau/\tau_c) - \Gamma], \quad (4.2a)$$

$$\Gamma = [1 - \exp(-\tau/\tau_c)] \sum_{k=1}^{\infty} \frac{(2k)!}{4^k (k!)^2} \exp(-2k\tau/\tau_c). \quad (4.2b)$$

Using Stirling's formula, $n! = (2\pi n)^{1/2} n^n \exp(-n)$, and replacing the sum by an integral, we can approximate Γ by

$$\Gamma = [1 - \exp(-\tau/\tau_c)] (2\tau/\tau_c)^{-1/2} \text{erf}[(2\tau/\tau_c)^{1/2}]. \quad (4.3)$$

When $\tau \ll \tau_c$, we can expand Eqs. (4.2a) and (4.3), obtaining for the isotropic case

$$D_x/D_s = \frac{1}{3} (\tau/2\tau_c)^{1/2} \quad (4.4)$$

or, in view of Eq. (3.1),

$$D_x = (\sigma/12) (D_s/\tau_c)^{1/2}. \quad (4.5)$$

Here σ should be interpreted as the persistence length of the chain. In Fig. 3 we show, for the isotropic case, how D_x/D_s varies from 0 to $\frac{1}{3}$ with increasing "persistence time" $\tau = \sigma^2/(2D_s)$ or decreasing residence time τ_c . The slow approach to the static limit is noteworthy. With $D_s \approx 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $\sigma \approx 30 \text{ nm}$, and τ_c a few microseconds, parameters typical for wormlike micelles, one has τ/τ_c of order 1.

B. Rouse model

In the Rouse model for the dynamics of a Gaussian chain in an isotropic system, the time correlation function for the normal coordinates is [9,10]

$$\langle \hat{x}(p,0) \hat{x}(p,k) \rangle = [\sigma^2 N / (6\pi^2 p^2)] \exp[-k\tau p^2 / (\tau_c N^2)], \quad (4.6)$$

with

$$\tau_c = \sigma^2 / (3\pi^2 D_c), \quad (4.7)$$

D_c being the translational diffusion coefficient of a chain segment of length σ . In terms of normal coordinates, the orientational time correlation function in Eq. (3.7) becomes

$$g(0,k) = [2\pi^2 / (\sigma^2 N^2)] \sum_{p=1}^N p^2 \langle \hat{x}(p,0) \hat{x}(p,k) \rangle. \quad (4.8)$$

Combination of Eqs. (4.6) and (4.8) yields, for the reduced correlation function,

$$\tilde{g}(0,k) = \frac{1}{N} \sum_{p=1}^N \exp\left(-\frac{k\tau p^2}{\tau_c N^2}\right) \approx \frac{\sqrt{\pi}}{2} \frac{\text{erf}[(k\tau/\tau_c)^{1/2}]}{(k\tau/\tau_c)^{1/2}}, \quad (4.9)$$

where, in the second step, we have approximated the sum by an integral. At short times ($k\tau \ll \tau_c$), Eq. (4.9) reduces to the exponential decay of Eq. (4.1). At long times ($k\tau \gg \tau_c$), however, Eq. (4.9) exhibits a slowly decaying tail of the form $[\pi\tau_c / (4k\tau)]^{1/2}$.

The macroscopic diffusion coefficient D_x for an isotropic chain with Rouse dynamics is obtained by substituting Eq. (4.9) into Eq. (3.10). A highly accurate closed-form approximation to this result is obtained by invoking Stirling's formula and converting the sum in Eq. (3.10b) to an integral, whereby

$$D_x/D_s = \frac{1}{3} \left\{ 1 - \frac{\sqrt{\pi}}{2} \frac{\text{erf}(\sqrt{\eta/2})}{\sqrt{\eta/2}} + \frac{\text{erf}(\sqrt{\eta})}{8\sqrt{\eta}} + \frac{\sqrt{\eta}}{4} \text{erfc}(\sqrt{\eta}) - \frac{\exp(-\eta)}{4\sqrt{\pi}} \right\}, \quad (4.10)$$

with $\eta = 2\tau/\tau_c$. For $\tau \ll \tau_c$, this expression reduces to

$$D_x/D_s = \frac{1}{6} (\tau/2\tau_c)^{1/2}, \quad (4.11)$$

which is one-half of the corresponding result Eq. (4.4) for the exchange model. In view of Eqs. (3.1) and (4.7), this may be expressed as

$$D_x = \frac{\pi}{4\sqrt{3}} (D_s D_c)^{1/2}, \quad (4.12)$$

showing that the macroscopic diffusion coefficient D_x is essentially the geometric mean of the curvilinear diffusion coefficient D_s and the chain segment diffusion coefficient D_c . Figure 4 shows how D_x varies with τ/τ_c for the Rouse model and also illustrates the accuracy of the approximations Eqs. (4.10) and (4.11). A comparison with Fig. 3 shows that the fast fluctuation limit is approached more slowly, as indeed expected for the distribution of orientational fluctuation modes in the Rouse model.

C. Nematic model

Finally, consider an anisotropic system of strongly coupled chains, whose collective reorientational dynamics can be described by the usual continuum mechanics of liquid

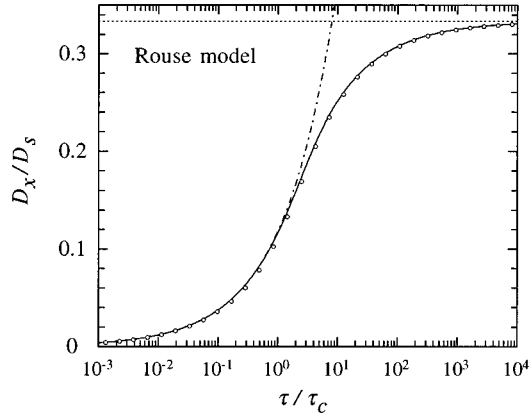


FIG. 4. Variation of the relative diffusion coefficient D_x/D_s for the Rouse model, with τ_c the correlation time for segment motion. The solid curve is the exact result Eqs. (3.10) and (4.9), while the circles represent the approximate result Eq. (4.10) and the broken curve the approximate result Eq. (4.11).

crystals [11,12]. This might be a nematic phase of polymers or long micelles. The laboratory-fixed x axis is taken to be along the optic (symmetry) axis of the uniaxial phase and the chain tangent \mathbf{u} defines the so-called local director [12].

In the theory of nematic director fluctuations, one focuses not on the longitudinal component $\zeta = \mathbf{u} \cdot \hat{\mathbf{x}}$ but on a transverse component $\rho = \mathbf{u} \cdot \hat{\mathbf{y}}$ of the local director. The time correlation function for either of the two independent Cartesian transverse director components is [11]

$$\langle \rho(0)\rho(k) \rangle = \langle \rho^2 \rangle \frac{\sqrt{\pi} \operatorname{erf}[(k\tau/\tau_c)^{1/2}]}{2 (k\tau/\tau_c)^{1/2}}, \quad (4.13)$$

with the viscoelastic cutoff time

$$\tau_c = \eta/Kq_c^2, \quad (4.14)$$

K being the (average) curvature elasticity of the phase, η the nematic viscosity, and $q_c = 2\pi/\lambda_c$, with λ_c the cutoff length below which the continuum description fails. Thus τ_c is the relaxation time for a director fluctuation mode of wavelength λ_c .

The mean-square fluctuation amplitude $\langle \rho^2 \rangle$ in Eq. (4.13) is related to the usual second-rank nematic order parameter

$$S = (3\langle \zeta^2 \rangle - 1)/2 \quad (4.15)$$

as

$$\langle \rho^2 \rangle = (1 - \langle \zeta^2 \rangle)/2 = (1 - S)/3. \quad (4.16)$$

If $\rho(k)$ is treated as a Gaussian random process, the orientational time correlation function in Eq. (3.7) becomes, to leading order in ρ [19],

$$g(0,k) = \langle \rho(0)\rho(k) \rangle^2. \quad (4.17)$$

The reduced correlation function thus becomes

$$\tilde{g}(0,k) = \frac{\pi}{4} \frac{\{\operatorname{erf}[(k\tau/\tau_c)^{1/2}]\}^2}{k\tau/\tau_c}. \quad (4.18)$$

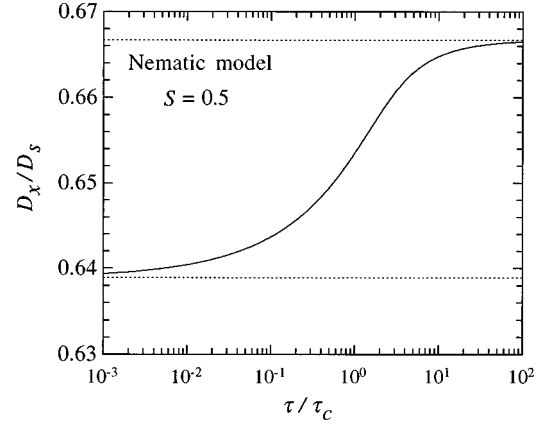


FIG. 5. Variation of the relative diffusion coefficient D_x/D_s for the nematic model, with τ_c the viscoelastic cutoff time. Even for a nematic order parameter S as low as 0.5, the variation of D_x due to director fluctuations is seen to be less than 5%.

At short times ($k\tau \ll \tau_c$), Eq. (4.18) reduces to an exponential decay $\exp(-2k\tau/\tau_c)$, while at long times ($k\tau \gg \tau_c$) it exhibits a slow algebraic decay $\pi\tau_c/(4k\tau)$. Furthermore, it follows from the preceding results that

$$\langle \zeta^2 \rangle = (1 + 2S)/3, \quad (4.19a)$$

$$\langle \zeta^2 \rangle - \langle \zeta \rangle^2 = [(1 - S)/3]^2. \quad (4.19b)$$

The macroscopic diffusion coefficient D_x for a particle on a chain undergoing nematic director fluctuations is now obtained by substituting Eqs. (4.18) and (4.19) into Eq. (3.10),

$$D_x/D_s = (1 + 2S)/3 - [(1 - S)/3]^2 \left[\frac{\pi}{4} \frac{\{\operatorname{erf}[(\tau/\tau_c)^{1/2}]\}^2}{\tau/\tau_c} - \Gamma \right], \quad (4.20a)$$

$$\Gamma = \frac{\pi}{4} \frac{\tau_c}{\tau} \sum_{k=1}^{\infty} \frac{(2k)!}{4^k (k!)^2} \left[\frac{\{\operatorname{erf}[(2k\tau/\tau_c)^{1/2}]\}^2}{2k} - \frac{\{\operatorname{erf}[(2k+1)\tau/\tau_c]^{1/2}\}^2}{2k+1} \right]. \quad (4.20b)$$

Figure 5 shows how D_x varies with τ/τ_c for the nematic model. The shape of the curve is the same for all values of S , although the limiting values are different. For a highly ordered nematic phase, D_x is of course insensitive to the director fluctuation dynamics (cf. Fig. 2).

V. CONCLUDING REMARKS

In the present work, we have examined theoretically the self-diffusion of a particle in a disordered one-dimensional geometry that fluctuates in time. Whereas spatial correlations of finite range have no effect on the projected diffusion coefficient D_x , temporal correlations are seen to be crucial. Our principal result Eq. (3.10) demonstrates how, on increasing the rate of orientational fluctuations, the ratio D_x/D_s of the projected and curvilinear diffusion coefficients increases from $\langle \zeta \rangle^2$ to $\langle \zeta^2 \rangle$.

In view of the wide applicability of diffusion and random-walk models, the present results may be useful in a variety of

contexts. In particular, they allow experimental diffusion data from solutions of polymers and wormlike micelles and from amphiphilic nematic or hexagonal liquid crystals to be analyzed in terms of the orientational distribution and dynamics of the polymers or amphiphilic aggregates. As illustrations of potential applications of this kind, we obtained in Sec. IV explicit results for D_x/D_s for three different dynamic models. When the chain dynamics are slower than the curvilinear diffusion ($D_c < D_s$), we found that the measured diffusion coefficient D_x is essentially the geometric mean of D_c and D_s . More elaborate dynamic models may be needed to describe real systems. For example, the exchange and Rouse models may be combined to incorporate the effect of amphiphile exchange in a relatively dilute solution of wormlike

micelles. At higher concentrations, other processes, such as chain reptation [20] and topological rearrangements [21], may need to be incorporated in the dynamic model.

While there are undoubtedly interesting applications of the present 1D results, the field of applications may be wider in the 2D case. In contrast to the present exact results, approximate methods must be used to treat diffusion on a random surface [22].

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