Nonlinear fluctuation effects in dilute polymer solutions in periodic flow

Ming J. Hsia
Department of Physics, Columbia University, New York, New York 10027

Ben O'Shaughnessy
Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, New York 10027

(Received 14 September 1992)

We study dilute solutions subjected to finite-amplitude periodic velocity-gradient fields of characteristics strength Ω, frequency ω, and vanishing time average. On time scales large compared to the flow period, fluctuations in particle position are equilibriumlike but with an effective diffusivity matrix $\tilde{\underline{D}}(\lambda)\equiv\underline{E}(\lambda)\underline{D}$, where $\underline{D}$ is the no-flow diagonal diffusion matrix and $\tilde{\underline{D}}$ depends nonlinearly on $\lambda\equiv\Omega/\omega$. We prove that $\det\tilde{\underline{D}} > \det\underline{D}$ and that $\mathrm{tr}\tilde{\underline{D}} \geq \mathrm{tr}\underline{D}$ for all flows of this class; physically, this implies that the rate of density decay and the rate of growth in size of a diffusing cloud of particles is always increased relative to no flow. This enhancement arises from the interaction of the flow with microscopic fluctuations and is an example of Taylor dispersion. When $1/\Omega$ and $1/\omega$ become comparable to the longest internal particle relaxation time the behavior changes since internal modes are excited. As an example, we consider a dilute polymer solution in a simplified "Rouse dynamics" treatment. Relative to the center of gravity the motion of a monomer decomposes into an "infinite" deterministic part arising from the periodic stretching of the chain plus fluctuations whose long-time form is characterized by the same effective diffusivity $\tilde{\underline{D}}$ as for the center of gravity. The mean-squared size of the chain is increased, relative to equilibrium, by the same factor $\mathrm{tr}\underline{E}/3$ as the diffusivity. Correlation functions amenable to measurement in dynamical scattering experiments are calculated; these provide direct measurement of the nonlinear $\tilde{\underline{D}}$.

PACS number(s): 05.40.+j, 36.20.Ey, 83.50.By

I. INTRODUCTION

When a liquid is subjected to macroscopic velocity gradients the fluctuating microscopic degrees of freedom describing the fluid particles interact with the macroscopic flow. The most familiar effect is viscosity for the case of a time-independent flow. Another kind of effect (Taylor dispersion [1]) concerns the fluctuation in particle position; flow and microscopic diffusion act together to modify the particle diffusivity. In this paper our objective is to investigate this interaction when the velocity-gradient field is time dependent and of finite amplitude. Given a flow which fluctuates in time one can identify at least two flow time scales: that characterizing the time dependence itself, and that associated with the *strength* of the flow, by which one means the typical magnitude of the velocity gradient whose dimensions are inverse time. To examine how such flow-fluctuation effects depend on these two time scales we choose the simple case of a dilute solution and we focus on the diffusivity of the dilute solute particles; the problem then reduces to one of independent particles. One expects a change in behavior when the flow time scales become small enough to compare to the time scales describing the internal scales of these dilute particles. We investigate this in the case when the particles are macromolecules, which are characterized by a continuum of internal modes.

Our motivations in choosing polymers are twofold. On the one hand they provide an opportunity to investigate the effects of internal mode excitations as mentioned above; on the other hand we are interested quite generally in the properties of polymer solutions under strong flows. Flowing polymer solutions exhibit unusual non-Newtonian effects when time scales associated with the flow are small enough to compare to characteristic polymer time scales. The majority of experimental and theoretical studies of flowing dilute polymer solutions have dealt with the *linear* flow regime in which the flow strength scale is much smaller than any polymer rate and so "drops out" of measured physical quantities (e.g., viscosity by definition is independent of flow strength, being the proportionality constant between stress and strain rate in the linear regime). In this case only the fluctuation time scale of the flow remains [e.g., ω^{-1} in measurements of frequency-dependent viscosity $\eta(\omega)$].

This paper includes a study of the case in which *both* time scales are relevant; thus the flow fluctuates as rapidly as, and the flow strength is as large as, the longest polymer relaxation rate. In this nonlinear regime polymer configurations are strongly distorted and a number of novel physical effects result from the interaction of this nonlinearity with the excited internal polymer modes. Our approach has been to begin with the simplest imaginable system from which to glean understanding of these effects, namely, a single polymer chain (corresponding to dilute polymer solutions) studied in the Rouse model [2] (which is the simplest available many-body dynamical polymer model) subjected to a periodic flow. This paper is a continuation of a study of this problem by one of the present authors and collaborators [3]. In this paper

"equal time" configurational quantities were calculated; here we calculate dynamical quantities such as the root-mean-square (rms) displacement of one monomer of the polymer and other dynamical correlation functions such as are relevant to scattering experiments.

There are at present few theoretical results on polymers in nonlinear time-dependent flows of the type described above. Aside from the fundamental interest, polymer chains experience velocity-gradient fields of this kind in turbulent fluids containing polymer additives. The study of such flows should therefore shed light on the phenomenon of polymer-induced drag reduction [4–8]. Since the present study is in the Rouse model, which neglects hydrodynamical and excluded-volume interactions between the monomers, our results are not directly comparable to experiment. However, the physics which emerges is nontrivial and understanding this relatively simple system is, with hindsight, a prerequisite for more sophisticated calculations. Among the results we obtain here perhaps the most intriguing is the entirely nonlinear effect of the enhanced diffusivity of a polymer segment. That is, we find that the fluctuation in the position of a segment, when averaged over the time scale of the flow, grows with time in the same manner as in equilibrium (no flow) except for an enhancement factor which derives from the stretching effect of the flow during one cycle. Fluctuations are amplified by the flow. Correspondingly, the steady-state size of the polymer has been shown to be enhanced by the same factor [3]. On longer time scales one finds that the polymer center-of-gravity diffusion is enhanced by this same factor; this effect has been previously observed in center-of-gravity diffusion of, for example, colloids in oscillatory shear flow [9].

Viscosity measurements constitute the major part of the existent experimental data on flowing dilute polymer solutions, both at zero frequency [10–13] and at finite frequency [14–17] and theoretical work has dealt mainly with the linear flow regimes corresponding to these experiments [18–22]. In the nonlinear regime there have been a number of experimental studies of strong flow effects in dilute systems using two-roll and four-roll mill devices [23,24] which create strongly extensional nonoscillatory flow environments for a polymer chain. At large flow strengths shear thinning has been observed [25], while in strong extensional flows the extensional viscosity is strongly enhanced [26].

Theoretical work on finite flow effects in dilute polymer solutions is very limited. The effects of strong extensional flow were investigated by de Gennes [27] and nonlinear, time-independent shear was considered in the works of Fixman [28] and Ottinger [29] which addressed shear thinning and by Rabin and Kawasaki [30] who investigated the suppression of excluded volume at high shear rates. Using scaling arguments, Rabin and co-workers [31] derived a shear-dependent form for the intrinsic viscosity which exhibits thinning and adapted this picture to include the effect of monomer-monomer ("internal") friction [32] on viscosity at high constant shears. Recently Baldwin and Helfand have [33] calculated the stresses induced by finite shear flow in a renormalization-group study in which excluded-volume and hydrodynamical effects were fully incorporated.

The structure of this paper is as follows. In Sec. II we consider the diffusion of a dilute species in oscillatory flow characterized by time scales far greater than any internal particle scales; in this case a Brownian particle treatment is valid. We prove that the diffusion is always enhanced by the flow in this simple system which describes the motion of the center of gravity of our polymer chain. In Sec. III we perform the analogous calculation for a polymer segment, i.e., the rms displacement of a segment is calculated as a function of time; for times greater than the flow time scale, the diffusion is enhanced similarly to the center of gravity. In Sec. IV the polymer chain dynamical scattering function is calculated; its form directly reflects the enhancement of diffusivity.

The most significant microscopic observations of polymer dynamics in dilute solution have been made in dynamical-light-scattering [34–36] and neutron-spin-echo [37–40] studies. Light scattering was used by Cottrell, Merill, and Smith [41] to study high-molecular-weight polyisobutylene solutions in shear flows, and Lindner and Oberthur [42,43] used small-angle neutron scattering to measure the coherent scattering function of polystyrene molecules in dilute solution subjected to shear flows. In these experiments the shear flows were constant in time; we are unaware of such dilute polymer scattering studies which have been performed in the presence of time-dependent flows. Our results suggest this would be of considerable interest; we discuss in Sec. VI which aspects are expected to remain in a more sophisticated treatment than that provided by the Rouse model. The results of Secs. II–IV are mainly concerned with the long-time regime (relative to the flow time scale) since this is the most universal regime and such time scales are anyway more likely to be accessible in experimental studies. In Sec. V these results are extended to the small-time regime, and we conclude with a discussion in Sec. VI.

II. ENHANCED DIFFUSIVITY: CENTER-OF-GRAVITY MOTION

In this paper we will study the behavior of a single particle (corresponding physically to a dilute solution) in a velocity field of the form

$$\mathbf{v}(\mathbf{r},t)=\Omega(t)\underline{A}\mathbf{r}\ , \tag{1}$$

where $\Omega(t)$ is periodic in time with period $2\pi/\omega$ and is written

$$\Omega(t)\equiv\Omega g(\omega t)\ . \tag{2}$$

The parameter Ω measures the flow strength and $g(u)$ is of order unity, has period 2π, and vanishing integral over one period:

$$\begin{aligned} &g(u+2\pi)=g(u)\ , \\ &\int_0^{2\pi} du\, g(u)=0\ . \end{aligned} \tag{3}$$

Our interest here is in flows whose time-averaged gradients vanish. As will be clarified below, a nonzero time average leads to qualitatively different behavior (e.g., the

notion of enhanced diffusivity ceases to have meaning). The time-independent matrix $\underline{A}$ represents the "shape" of the flow. All results will be phrased for arbitrary traceless $\underline{A}$, though as specific examples we will often treat the following two particular forms:

$$\underline{A}=\begin{bmatrix}1 & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & -\frac{1}{2}\end{bmatrix} \tag{4}$$

representing pure extension, and

$$\underline{A}=\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \tag{5}$$

representing simple shear.

In this section we consider the case when $\Omega,\omega \ll 1/\tau_0$ where τ_0 is the longest relaxation time of the particle (see Fig. 6). Then the particle's center of gravity $\mathbf{R}_G$ obeys the simple Brownian particle Langevin equation (plus flow)

$$\frac{d\mathbf{R}_G}{dt}=\Omega(t)\underline{A}\mathbf{R}_G+\mathbf{f}_G(t)\ , \tag{6}$$

where the Gaussian random force $\mathbf{f}_G(t)$ has zero mean and is correlated as

$$\langle \mathbf{f}_G(t)\mathbf{f}_G(t')\rangle=\underline{I}\frac{2}{\zeta_G}\delta(t-t')\ . \tag{7}$$

$1/\zeta_G$ is the center of gravity mobility and $\underline{I}$ the unit matrix (we work in units where $k_BT=1$). In terms of the initial condition at t_0, namely, $\mathbf{R}_G(t_0)$, the solution is

$$\mathbf{R}_G(t)=\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\mathbf{R}_G(t_0)+\int_{t_0}^{t}dt'\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1}\underline{f}_G(t')\ , \tag{8}$$

where $\underline{\Gamma}_t$ is the (matrix) propagator from time 0 to time t for the deterministic dynamics of a fluid element in the flow field $\Omega(t)\underline{A}\mathbf{r}$ (i.e., no random force $\mathbf{f}_G$), and $\underline{\Gamma}_t^{-1}$ is its inverse,

$$\underline{\Gamma}_t\equiv e^{\underline{A}\int_0^t dt'\Omega(t')},\quad \underline{\Gamma}_t^{-1}=e^{-\underline{A}\int_0^t dt'\Omega(t')}\ . \tag{9}$$

Note that the time-dependent flow breaks the time translational invariance of the problem; hence the propagator between two general times t' and t, which equals $\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1}$, depends on *both* times. $\underline{\Gamma}_t$ refers specifically to $t=0$ as the initial time. Since $\Omega(t)$ is periodic and its time integral over one period $2\pi/\omega$ is zero [Eq. (3)], it follows that $\underline{\Gamma}_t$ is itself periodic. This is an important property which leads to the existence of an effective diffusivity; the absence of this property in the case of a nonvanishing time average of $\Omega(t)$ would induce qualitatively different behavior.

A comment is necessary at this point on the choice of lower limit, $t'=0$, in the integral in the exponent defining $\underline{\Gamma}_t$ above. The choice is arbitrary, in that observables are unaffected; however, a natural rule is that the lower limit t_l obeys $\langle \int_{t_l}^{t}du\, g(u)\rangle_t=0$, where $\langle\ \rangle_t$ denotes time average over one period. Throughout this paper we assume a time coordinate chosen such that $t_l=0$ obeys this criterion.

From Eq. (8) the two-time dyad correlation function is the sum of a deterministic term and a diffusive term (the second on the right-hand side),

$$\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle$$
$$=(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{R}_G(t_0)(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{R}_G(t_0)+\int_{t_0}^{t}dt''\int_{t_0}^{t}dt'\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1}\langle \mathbf{f}_G(t')\mathbf{f}_G(t'')\rangle(\underline{\Gamma}_t\underline{\Gamma}_{t''}^{-1})^T\ , \tag{10}$$

where we have used the vanishing of the mean of $\mathbf{f}_G$ and the fact that $\underline{B}\mathbf{x}=\mathbf{x}\underline{B}^T$ for any matrix $\underline{B}$ and vector $\mathbf{x}$. There is no averaging over $\mathbf{R}_G(t_0)$ in Eq. (10); these are the statistics for a given initial particle position. Using Eq. (7) one finds that this diffusive term in Eq. (10) is given by

$$\underline{\Gamma}_t\left\{\frac{2}{\zeta_G}\int_{t_0}^{t}dt'\underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_{t'}^{-1})^T\right\}\underline{\Gamma}_t^T\ . \tag{11}$$

We seek the form of this correlation function for times much larger than the flow period, $t-t_0\gg\omega^{-1}$. Let us define the effective diffusivity matrix $\tilde{\underline{D}}$ as follows:

$$\tilde{\underline{D}}\equiv\lim_{t\to\infty}\frac{1}{\zeta_G}\frac{1}{t-t_0}\int_{t_0}^{t}dt'\underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_{t'}^{-1})^T$$
$$=\frac{1}{\zeta_G}\langle\underline{\Gamma}_t^{-1}(\underline{\Gamma}_t^{-1})^T\rangle_t\ , \tag{12}$$

where $\langle\ \rangle_t$ denotes a uniform time average over one period of the flow $2\pi/\omega$. We name the time average appearing in Eq. (12) the "enhancement tensor" $\underline{E}$:

$$\underline{E}\equiv\langle\underline{\Gamma}_t^{-1}(\underline{\Gamma}_t^{-1})^T\rangle_t\equiv\frac{\omega}{2\pi}\int_0^{2\pi/\omega}dt\,\underline{\Gamma}_t^{-1}(\underline{\Gamma}_t^{-1})^T\ . \tag{13}$$

Since $\underline{\Gamma}_t$ is positive, bounded, and periodic, the limit of Eq. (12) exists and equals a finite positive constant independent of the initial value t_0. For large times $t-t_0$ we thus have

$$\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle=(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{R}_G(t_0)(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{R}_G(t_0)+2\underline{\Gamma}_t\tilde{\underline{D}}(t-t_0)\underline{\Gamma}_t^T\ , \tag{14}$$

with small corrections of order $\underline{\Gamma}_t \tilde{\underline{D}} \omega^{-1} \underline{\Gamma}_t^T$. In the absence of flow ($\underline{\Gamma}_t = \underline{I}$) this reduces to the usual expression $2\underline{D}(t-t_0)$ for the fluctuation in the center of gravity where $\underline{D}$ is the diffusivity matrix in the absence of flow. When flow is switched on the tensor $\underline{E}$ represents the enhancement of $\tilde{\underline{D}}$ relative to $\underline{D}$:

$$\tilde{\underline{D}} = \underline{E}\,\underline{D}, \quad \underline{D} \equiv \underline{I}/\zeta_G \ . \tag{15}$$

To connect with the usual diffusion constant D defined in terms of the mean-square displacement, which equals the trace of the dyad, observe that this latter is given by $3/\zeta_G$, the standard result. Note that Eq. (12) guarantees that $\tilde{\underline{D}}$ is always symmetric and positive definite [equivalently, see Eq. (16) below]. We emphasize also the importance of the vanishing of the time integral of the flow gradient field $\Omega(t)$ [Eq. (3)], without which $\tilde{\underline{D}}$ would not be defined; in this case the second term in Eq. (14) would grow faster than linearly with time at a rate determined by the time-averaged value of $\Omega(t)\underline{A}$. As a result the limit of Eq. (12) no longer exists. In Appendix A we consider this case, the physics of which for long times is essentially that of a time-independent gradient field, and we demonstrate that the growth in time of the fluctuation in particle position is either polynomial (with degree greater than unity) or exponential. In practice a small time average [relative to the magnitude of the fluctuating part of $\Omega(t)$] will not upset the enhanced diffusive behavior for smaller times; at sufficiently large times, however, this will yield to the polynomial or exponential behavior.

The correlation function of Eq. (14) describes the statistics of the displacement of a cloud of independent diffusing particles relative to its position at time t_0. At t_0 the cloud is a point contained in the fluid element at $\mathbf{R}_G(t_0)$. The deterministic first term is the dyad formed from the displacement of this fluid element and equals the dyad formed from the mean displacement of particles belonging to the cloud [take the average of Eq. (8)]. The diffusive second term describes the shape and size of the cloud itself, relative to its center of gravity, as it gets deformed by the flow and by the diffusion of the particles which comprise it. Indeed, this term is the fluctuation in the position of particles in the cloud relative to their initial position, being the matrix of second cumulants of products of the different components of the cloud displacements:

$$\begin{aligned}\langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)] \rangle_c \equiv & \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)] \rangle \\ & - \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)] \rangle \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)] \rangle = 2\underline{\Gamma}_t \tilde{\underline{D}}(t-t_0)\underline{\Gamma}_t^T \ .\end{aligned} \tag{16}$$

Now the inner part of the fluctuation matrix, $\tilde{\underline{D}}(t-t_0)$, represents the shape and size of the cloud at "reference times" which are integer multiples of $2\pi/\omega$; this grows linearly with time and with a *flow-enhanced diffusivity* $\tilde{\underline{D}}$. We will prove below that the diffusivity is indeed always *enhanced* by an incompressible flow. The operator $\underline{\Gamma}_t \{\ \} \underline{\Gamma}_t^T$ acts on this inner part to give the fluctuation at times which are not integer multiples of $2\pi/\omega$. This operator effects the periodic deformation of the cloud in the flow, and represents a deterministic effect in addition to the motion of the center of gravity of the cloud. Thermal fluctuations disperse the cloud and the deterministic flow then periodically deforms this dispersion. In the next section, when we come to consider the displacement of one unit of the polymer for short times, we will find similar physics but also subtle differences. A unit is attached to a chain which is itself deforming in the flow, somewhat like the deforming cloud. However, any one diffusing particle does not physically interact with its cloud, in contrast to a unit which is actually attached to a polymer chain.

Let us now justify our use of the expression "enhancement of diffusivity" by proving that the fluctuation in the mean-square displacement of a particle (for times which are large compared to the flow period) is greater than or equal to the same quantity in the absence of flow. From Eq. (16) this fluctuation equals $2\,\mathrm{tr}\underline{\Gamma}_t \tilde{\underline{D}}(t-t_0)\underline{\Gamma}_t^T$ where tr denotes the trace operation; without flow this becomes $2\,\mathrm{tr}\underline{D}(t-t_0)$. First we demonstrate that $\mathrm{tr}\tilde{\underline{D}} \geq \mathrm{tr}\underline{D}$. Consider any $d \times d$ matrix $\underline{X}$ (we have a flow in d dimensions in mind). Define $\langle \cdots \rangle \equiv (1/d)\sum_{i=1}^{i=d} \{ \cdots \}$, and let the eigenvalues of the matrix $e^{\underline{X}} e^{\underline{X}^T}$ be $\{e^{\mu_i}\}_{i=1}^{i=d}$. Note that this matrix $e^{\underline{X}} e^{\underline{X}^T}$, being of positive-definite form, has eigenvalues which may always be written in this form for real μ_i. Its determinant is given by

$$\begin{aligned}\det e^{\underline{X}} e^{\underline{X}^T} &= (\det e^{\underline{X}})^2 \\ &= e^{2\,\mathrm{tr}\underline{X}} \ ,\end{aligned} \tag{17}$$

where we have used the fact that the determinant of a matrix equals the determinant of its transpose. The use of Eq. (17) and the general result $\langle e^x \rangle \geq e^{\langle x \rangle}$ allows the establishment of the following inequality:

$$\begin{aligned}\mathrm{tr} e^{\underline{X}} e^{\underline{X}^T} \equiv d\langle e^{\mu_i} \rangle &\geq d e^{\langle \mu_i \rangle} \\ &= d \left[\prod_{i=1}^{i=d} e^{\mu_i} \right]^{1/d} \\ &= d(\det e^{\underline{X}} e^{\underline{X}^T})^{1/d} \\ &= d e^{(2/d)\mathrm{tr}\underline{X}} \ .\end{aligned} \tag{18}$$

From Eq. (13), $\underline{E}$ is the time average of a matrix of the form $e^{\underline{X}} e^{\underline{X}^T}$ with $\underline{X}$ being minus the time integral of the flow gradient matrix $\Omega(t)\underline{A}$. When the flow is incompressible this matrix is traceless; noting that the time averaging and trace operations commute, Eq. (18) then implies that $\mathrm{tr}\underline{E} \geq \mathrm{tr}\underline{I}$, and thus from Eq. (15)

$$\mathrm{tr}\tilde{\underline{D}} \geq \mathrm{tr}\underline{D} \quad \text{(incompressible flow)} \ . \tag{19}$$

This result implies through Eq. (16) that at times which are integer multiples of the flow period $2\pi/\omega$ the fluctua-

tion in cloud displacement is enhanced. In fact this is true for *all* times, since from Eqs. (16), (15), and (12) one can write

$$\langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle_c = 2\underline{D}\langle \underline{\Gamma}_t\underline{\Gamma}_{t'}(\underline{\Gamma}_t\underline{\Gamma}_{t'})^T\rangle_{t'}$$
$$= 2\underline{D}\langle e^{\underline{A}\int_{t'}^{t}\Omega} e^{\underline{A}^T\int_{t'}^{t}\Omega}\rangle_{t'} . \tag{20}$$

The quantity in the time-averaging brackets is again of the form $e^{\underline{X}}e^{\underline{X}'}$ with X traceless; its trace is thus greater than or equal to $\mathrm{tr}\underline{I}$ and we establish that the fluctuation in displacement is enhanced at all times,

$$\langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]^2\rangle_c^{\text{compressible flow}} \geq \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]^2\rangle_c^{\text{no flow}} . \tag{21}$$

Consider some particular cases now. For simple extensional flow, the deterministic flow propagator and the effective diffusivity matrices are diagonal, Eqs. (12) and (9),

$$\underline{\Gamma}_t = \begin{bmatrix} e^{\lambda\int_0^{\omega t} du\, g(u)} & 0 & 0 \\ 0 & e^{-(1/2)\lambda\int_0^{\omega t} du\, g(u)} & 0 \\ 0 & 0 & e^{-(1/2)\lambda\int_0^{\omega t} du\, g(u)} \end{bmatrix} \tag{22}$$

and

$$\underline{\tilde{D}} = \underline{D}\begin{bmatrix} \langle e^{-2\lambda\int_0^u g}\rangle_u & 0 & 0 \\ 0 & \langle e^{\lambda\int_0^u g}\rangle_u & 0 \\ 0 & 0 & \langle e^{\lambda\int_0^u g}\rangle_u \end{bmatrix} , \tag{23}$$

where $\lambda \equiv \Omega/\omega$ measures the degree of nonlinearity of the flow [3]. Here

$$\langle \cdots \rangle_u \equiv \frac{1}{2\pi}\int_0^{2\pi} du\{\cdots\} \tag{24}$$

denotes time averaging over one dimensionless cycle (of length 2π) of the flow. Using $\langle e^x\rangle_u \geq 1+\langle x\rangle_u$ on each of the elements of $\underline{\tilde{D}}$ in Eq. (23), one immediately verifies the enhancement $\mathrm{tr}\underline{\tilde{D}} > \mathrm{tr}D$ for nonzero λ. The emergence of λ as the natural measure of the nonlinearity of the flow and of the degree of enhancement is a general feature. λ parametrizes the net strain in one flow cycle (i.e., a strain rate $\sim\Omega$ persisting for a time $\sim\omega^{-1}$). This strain, which in the extensional flow case is exponential in λ, is the flow-induced fractional increase in the diffusive "blur" in the position of the center of gravity which occurs in one flow cycle. It is this "blur straining" averaged over one cycle which enhances the diffusivity. On time scales beyond one flow cycle the diffusion does not feel the stretching effect of the changing flow and develops linearly in time as in the no-flow case, albeit with an enhanced coefficient.

It is important to realize that these effects are entirely *nonlinear* in λ, as can be seen by expanding $\underline{\tilde{D}}$, Eq. (12), in powers of $\underline{A}$ and $\underline{A}^T$. After time-averaging a term of nth order is proportional to $\lambda^n\langle(\int_0^u g)^n\rangle_u$; thus terms linear in λ are linear in $\underline{A}$ or $\underline{A}^T$ and are annihilated by the trace operation. There is no enhancement of diffusivity to order λ.

In fact the enhancement in the trace proved above can be deduced from a stronger inequality on the determinant of $\underline{E}$ (we have presented the weaker inequality above on account of its relative simplicity). From this inequality we will deduce that the *density* of a diffusing cloud is *reduced* by the flow. We will make use of the Hölder inequality [44],

$$\int dx \left[\prod_{i=1}^{N} f_i(x)\right] \leq \prod_{i=1}^{N}\left[\int dx\, f_i^{q_i}(x)\right]^{1/q_i}, \quad \underline{N}\geq 2 ,$$
$$\sum_{i=1}^{N}\frac{1}{q_i}=1, \quad q_i>0 , \tag{25}$$

where $f_i(x)$ takes non-negative values and the equality is only true when at least one of the $\{f_i(x)\}$ is zero or all of the $\{f_i(x)\}$ are proportional to each other. Since $\underline{E}$ is positive definite we can express $(\det\underline{E})^{-1/2} = \pi^{-d/2}\int d^dx \exp\{-x\underline{E}x\}$, and write $\underline{E} = (1/T)\sum_{t'=1}^{T}\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1^T}$, i.e., we have discretized time into T units of size Δt per period, $T\equiv 2\pi/(\omega\Delta t)$. Using Eq. (25), with $N=q_i=T$ and $f_i(x)=\exp\{-x\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1^T}x/T\}$, and noting that $\det\underline{\Gamma}_t = \exp\{\mathrm{tr}\Omega\int_0^t\underline{A}\}=1$ since $\mathrm{tr}\underline{A}=0$, we find that

$$\int d^dx\, e^{-x\underline{E}x} \leq \prod_{t'=1}^{T}\left[\int d^dx\, e^{-x\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1^T}x}\right]^{1/T}$$
$$= \prod_{t'=1}^{T}\{\pi^{d/2}[\det(\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1^T})]^{-1/2}\}^{1/T}$$
$$= \pi^{d/2} , \tag{26}$$

where we have used $\det(\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1^T}) = [\det(\underline{\Gamma}_{t'}^{-1})]^2 = 1$ which follows since $\det\underline{\Gamma}_t = \exp\{\mathrm{tr}\Omega\int_0^t\underline{A}\}$ and $\mathrm{tr}\underline{A}=0$ for these incompressible flows. Thus we conclude that $(\det\underline{E})^{-1/2}\leq 1$ or

$$\det\underline{E} \geq 1 . \tag{27}$$

This inequality is the central result of this section. In fact the inequality is *strict* with the exception of purely rotational flows for which $\underline{A}+\underline{A}^T=0$ [only then are all of the $\{f_i(x)\}$ the same]. Equation (27) also implies a similar inequality on the trace

$$\mathrm{tr}\underline{E} \geq d \ , \tag{28}$$

which follows since $\mathrm{tr}\underline{E}/d \geq (\det\underline{E})^{1/d}$ which is the statement (for our positive definite $\underline{E}$) of the fact that the arithmetic mean of a set of positive-definite numbers exceeds their geometric mean. Equation (28) is of course equivalent to our previously derived inequality, Eq. (19). As we have shown previously, since $\tilde{\underline{D}}=\underline{E}\,\underline{D}$ where $\underline{D}=\underline{I}/\zeta_G$ is the no-flow diagonal diffusivity matrix we have $\mathrm{tr}\{\underline{\Gamma}_t\tilde{\underline{D}}\,\underline{\Gamma}_t^T\} \geq d[\det(\underline{\Gamma}_t\tilde{\underline{D}}\,\underline{\Gamma}_t^T)]^{1/d}=d(\det\tilde{\underline{D}})^{1/d} > d(\det\underline{D})^{1/d}=\mathrm{tr}\underline{D}$. From Eq. (16) this implies that the fluctuation in particle position is enhanced by the flow, i.e., the mean-square size of the cloud is greater. Note that $\tilde{\underline{D}}$ is no longer diagonal, i.e., flow destroys isotropy; therefore the inequality on the trace does not in itself imply that the flow reduces the cloud density, since displacement is in general enhanced in some directions and suppressed in others. To demonstrate reduced density, we note also from the Langevin equation that $\mathbf{R}_G(t)$ is Gaussian and thus the density $\tilde{\rho}_t$ at the center of gravity of the cloud $\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\mathbf{R}_G(t_0)$ is simply the normalization of this Gaussian whose correlation matrix appears in Eq. (14): $\tilde{\rho}_t=[\det\{4\pi\underline{\Gamma}_t\tilde{\underline{D}}(t-t_0)\underline{\Gamma}_t^T\}]^{-1/2}$. Then since $\det\underline{\Gamma}_t=1$ we have $\tilde{\rho}_t/\rho_t=(\det\underline{E})^{-1/2}\leq 1$ where ρ_t is the equivalent quantity without flow. Thus the flow reduces the cloud density.

This increased rate of density decay is in fact related to an increase in the entropy production due to the particle diffusion as follows. For nonequilibrium processes the entropy production rate σ for a flow field $\mathbf{v}$ is generally given by [45] (ρ is the particle number density of the solution)

$$\frac{d}{dt}\int \rho s\, dV = -\int \frac{\Pi^T:\nabla\mathbf{v}}{T}dV - \int \frac{\underline{j}\cdot\nabla\mu}{T}dV - \int \frac{(\underline{j}_q-\mu\underline{j})\cdot\nabla T}{T^2}dV \ , \tag{29}$$

where s is the entropy per particle, Π is the stress tensor, $\underline{j}$ the solute particle number flux, μ the chemical potential, T the temperature, and $\underline{j}_q$ the heat flux. In the present case of uniform T the third term vanishes. Let us consider the contribution from the diffusive motion (i.e., in addition to the stress contribution represented by the first term), which we name $\sigma=\int(\underline{j}\cdot\nabla\mu)/T\,dV$. Now the current $\underline{j}$ is given by $\underline{j}=-\rho D\nabla C$ where C is the ratio of particle number densities of solute to solution. Now C is proportional to number density of solute particles each of which obeys our Langevin equation, and so has Gaussian distribution of the form below (M is the total number of solute particles):

$$C(\mathbf{R},t;\mathbf{R}_0,t_0)=\frac{M}{\rho}\frac{1}{\{(4\pi)^3\det[\tilde{\underline{D}}(t-t_0)+\Sigma_0]\}^{1/2}}e^{(\mathbf{R}-\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\mathbf{R}_0)\{4\underline{\Gamma}_t[\tilde{\underline{D}}(t-t_0)+\Sigma_0]\underline{\Gamma}_t^T\}^{-1}(\mathbf{R}-\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\mathbf{R}_0)} \tag{30}$$

for the case of an initially Gaussian distribution with dispersion matrix Σ_0. The dispersion from a δ-function initial condition is obtained from Eq. (14); one then simply adds dispersions to obtain that in Eq. (30). Using this form in $\mu=T\ln C+\Psi(T,p)$ (the ideal solution result with p being the pressure) gives [$\Sigma_t=\tilde{\underline{D}}(t-t_0)+\Sigma_0$ is the dispersion at time t]

$$\begin{aligned}\sigma &= \int d^3R\ \frac{\nabla_{\mathbf{R}}C\underline{D}\nabla_{\mathbf{R}}C}{C} \\ &= \frac{M}{[\det(4\pi\Sigma_t)]^{1/2}}\int d^3X\,\nabla_{\underline{X}}\left[\frac{\underline{X}\Sigma_t^{-1}\underline{X}}{4}\right]\underline{\Gamma}_t^{-1}\underline{D}\,\underline{\Gamma}_t^{-1^T}\nabla_{\underline{X}}\left[\frac{\underline{X}\Sigma_t^{-1}\underline{X}}{4}\right]e^{-(1/4)\underline{X}\Sigma_t^{-1}\underline{X}} \\ &= \frac{M}{[\det(4\pi\Sigma_t)]^{1/2}}\int d^3X\,\underline{X}(\Sigma_t^{-1^T}\underline{\Gamma}_t^{-1}\underline{D}\,\underline{\Gamma}_t^{-1^T}\Sigma_t^{-1})\underline{X}e^{-(1/4)\underline{X}\Sigma_t^{-1}\underline{X}} \\ &= \frac{M}{2}\mathrm{tr}[\Sigma_t^{-1^T}\underline{\Gamma}_t^{-1}\underline{D}\,\underline{\Gamma}_t^{-1^T}] \ ,\end{aligned} \tag{31}$$

where we substituted $\underline{X}=\underline{\Gamma}_t^{-1}\mathbf{R}-\underline{\Gamma}_{t_0}^{-1}\mathbf{R}_0$ and we used the identity $\int d^dX\,\underline{X}\,\underline{B}\,\underline{X}\exp\{-\underline{X}\,\underline{A}\,\underline{X}\} = \frac{1}{2}[\det(\pi\underline{A})]^{1/2}\mathrm{tr}[\underline{B}\,\underline{A}^{-1}]$. Thus the change in entropy (from this term) in the time interval (t_0,t) is approximately given by (assuming $t-t_0\gg\omega^{-1}$)

$$\begin{aligned}\Delta S=\int_{t_0}^t dt\,\sigma &\approx \frac{M}{2}\int_{t_0}^t dt'\mathrm{tr}[\Sigma_t'^{-1^T}\tilde{\underline{D}}]=\frac{M}{2}\mathrm{tr}\int_{t_0}^t dt'[(t-t_0)\underline{I}+\Sigma_0\tilde{\underline{D}}^{-1}]^{-1} \\ &= \frac{M}{2}\mathrm{tr}\ln[\underline{I}+\tilde{\underline{D}}^{-1}\Sigma_0(t-t_0)]^{-1} \\ &= \frac{M}{2}\ln\left\{\frac{\det[\Sigma_0+(t-t_0)\tilde{\underline{D}}^{-1}]}{\det(\Sigma_0)}\right\} \\ &= -M\ln\{[\det(4\pi\Sigma_0)]^{1/2}\tilde{\rho}_t\}=M\ln[\rho_0/\tilde{\rho}_t] \ ,\end{aligned} \tag{32}$$

where $\underline{\Gamma}_t^{-1}\underline{D}\,\underline{\Gamma}_t^{-1^T}$ was preaveraged to give $\tilde{\underline{D}}$ which is justified due to the slow variation in time of $\underline{\Sigma}_t^{-1^T}$ (note $\underline{\Sigma}_t^{-1^T}$ has already been preaveraged). For long time (relative to the diffusion time associated with Σ_0) we find that the total change in entropy per particle at time t for an initial (t_0) patch of density ρ_0 is given by $\Delta S \approx \ln[\rho_0/\tilde{\rho}_t]$ for time differences much greater than the flow period. Then since $\tilde{\rho}_t$ is less than the value it would have without flow, thus ΔS is greater than it would have been without flow when compared at the same time.

Let us now consider several particular cases. A simple specific example of the general extensional flow of Eqs. (23) and (22) is that of sinusoidal extensional flow $g(u)=\cos u$:

$$\tilde{\underline{D}}=\underline{D}\begin{bmatrix}\langle e^{-2\lambda\sin u}\rangle_u & 0 & 0\\ 0 & \langle e^{\lambda\sin u}\rangle_u & 0\\ 0 & 0 & \langle e^{\lambda\sin u}\rangle_u\end{bmatrix}, \tag{33}$$

where $\langle e^{-2\lambda\sin u}\rangle_u = I_0(2\lambda)$ is the modified zeroth-order Bessel function of pure imaginary argument [46].

In the simple shear case, Eq. (5), one has $\underline{A}^2=0$ so $e^{\alpha\underline{A}}=1+\alpha\underline{A}$ for constant α. Then the deterministic flow operator $\underline{\Gamma}_t$, Eq. (9), is

$$\underline{\Gamma}_t=\begin{bmatrix}1 & \lambda\int_0^{\omega t}du\,g(u) & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}, \tag{34}$$

and the effective diffusivity matrix

$$\tilde{\underline{D}}=\underline{D}\begin{bmatrix}1+\lambda^2\langle(\int_0^u g)^2\rangle_u & -\lambda\langle\int_0^u g\rangle_u & 0\\ -\lambda\langle\int_0^u g\rangle_u & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$=\underline{D}\begin{bmatrix}1+\lambda^2 & \langle(\int_0^u g)^2\rangle_u & 0 & 0\\ & 0 & 1 & 0\\ & 0 & 0 & 1\end{bmatrix}, \tag{35}$$

where we have used the property $\langle\int_0^u g\rangle_u=0$ (as enforced by our choice of lower time limit). The trace of the matrix multiplying $\underline{D}$ is manifestly greater than 3 for nonzero λ. Observe how in pure shear the exact flow-induced part of the fluctuation appears additively as a quadratic term in the natural parameter λ. Note also that $\tilde{\underline{D}}$ in general describes an anisotropic dispersion of the cloud whose diffusion in certain directions is enhanced and in others is suppressed.

In simple sinusoidal shear flow one has

$$\tilde{\underline{D}}=\underline{D}\begin{bmatrix}1+\frac{\lambda^2}{2} & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}. \tag{36}$$

For a general periodic flow a convenient starting point for calculating the enhancement tensor $\underline{E}$ of Eq. (13) (which determines $\tilde{\underline{D}}$) is the fact that the real velocity gradient matrix $\Omega(t)\underline{A}$ can be expressed in Jordan canonical form under a suitable transformation. That is, there exists a nonsingular matrix $\underline{P}$ such that $\underline{A}=\underline{P}(\Lambda+\underline{N})\underline{P}^{-1}$ where Λ is the diagonal matrix of the eigenvalues of $\underline{A}$ (with each eigenvalue repeated as many times as it is degenerate) and $\underline{N}$ is nilpotent. The procedure for finding the Jordan canonical form of a matrix (i.e., for deriving $\underline{P}$) is standard [47]. Thus $e^{\underline{A}}=\underline{P}e^{\Lambda+\underline{N}}\underline{P}^{-1}=\underline{P}[e^{\Lambda}e^{\underline{N}}]\underline{P}^{-1}$ since Λ and $\underline{N}$ commute. Since Λ is diagonal e^{Λ} is easy to evaluate, and with $\underline{N}$ being nilpotent $e^{\underline{N}}$ is a polynomial in $\underline{N}$. Replacing $\underline{A}\to\int\Omega\underline{A}$ one can thus obtain $\underline{\Gamma}_t$ and then $\underline{E}$ from Eq. (13).

The two-dimensional case, for which $\tilde{\underline{D}}$ can be explicitly calculated for arbitrary flow, serves as a convenient example. In this case for incompressible flow $\underline{A}$ has the form

$$\underline{A}=\begin{bmatrix}a & b\\ c & -a\end{bmatrix} \tag{37}$$

so Λ has diagonal elements $\pm(a^2+bc)^{1/2}$. One finds that, provided $a^2+bc\neq 0$, $\underline{N}=0$ and the elements of $\underline{P}$ are $\underline{P}_{11}=\underline{P}_{22}=1$, $\underline{P}_{12}=[-(a^2+bc)^{1/2}+a]/c$, $\underline{P}_{21}=[(a^2+bc)^{1/2}-a]/b$. This leads to

$$\underline{\Gamma}_t=\begin{bmatrix}\cosh\theta+a\frac{\sinh\theta}{\theta} & b\frac{\sinh\theta}{\theta}\\ c\frac{\sinh\theta}{\theta} & \cosh\theta-a\frac{\sinh\theta}{\theta}\end{bmatrix},$$

$$\underline{\Gamma}_t^{-1}=\begin{bmatrix}\cosh\theta-a\frac{\sinh\theta}{\theta} & -b\frac{\sinh\theta}{\theta}\\ -c\frac{\sinh\theta}{\theta} & \cosh\theta+a\frac{\sinh\theta}{\theta}\end{bmatrix},$$

where $\theta^2(t)\equiv(a^2+bc)\Omega^2(t)$. With the flow operator evaluated, it is simple to obtain $\underline{E}$ from Eq. (13). A special case is when the determinant of $\underline{A}$ vanishes, $a^2+bc=0$, which would render $\underline{P}$ as defined above noninvertible; then $\underline{A}$ itself is nilpotent ($\underline{A}^2=0$) so $\Lambda=0$, and $\underline{P}$ changes form. Thus $\underline{\Gamma}_t=\exp\int_0^t\Omega\underline{A}=1+\int_0^t\Omega\underline{A}$. Note that this matches the expression in Eq. (38) in the limit $\theta\to 0$.

What are the experimental predictions of our theory? A number of experimental techniques are suited to measuring the effective diffusivity matrix. For example, light scattering on solutions subjected to strong periodic flow which contain diffusing particulate scattering centers furnishes a direct probe of the dynamic structure factor $S(\mathbf{k},t)$, namely, the two-time correlation function of the $\mathbf{k}$th Fourier amplitude of the particle density. Defining $S(\mathbf{k},t)$ to be the correlation function per particle, using Eq. (14) and the fact that $\mathbf{R}_G(t)$ is Gaussian, one finds for an N-particle system in which the ith particle is located at $\mathbf{R}_G^i$ (for $\mathbf{k}\neq\mathbf{0}$)

$$
\begin{aligned}
S_G(\mathbf{k},t) &= \frac{1}{N}\left\langle \sum_{ij}^{N} e^{i\mathbf{k}[\mathbf{R}_G^i(t)-\mathbf{R}_G^i(t_0)]} \right\rangle \\
&= \frac{1}{N}\sum_{i}^{N} \langle e^{i\mathbf{k}[\mathbf{R}_G^i(t)-\mathbf{R}_G^i(t_0)]} \rangle \\
&= \langle e^{i\mathbf{k}(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{R}_G(t_0)} \rangle_{\mathbf{R}_G(t_0)} \langle e^{i\mathbf{k}\int_{t_0}^{t} dt'\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1}\mathbf{f}_G(t')} \rangle_{\mathbf{f}_G} \\
&= \frac{(2\pi)^3}{V}\delta(\mathbf{k}[\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I}])e^{-(1/2)\mathbf{k}\underline{\Gamma}_t\tilde{\underline{D}}(t-t_0)\underline{\Gamma}_{t_0}^{T}\mathbf{k}} \\
&= \frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))[\det(\underline{\Gamma}_{t_0}\underline{\Gamma}_t^{-1})]e^{-(1/2)\mathbf{k}\underline{\Gamma}_{t_0}\tilde{\underline{D}}(t-t_0)\underline{\Gamma}_{t_0}^{T}\mathbf{k}} \\
&= \frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))e^{-(1/2)\mathbf{k}\underline{\Gamma}_{t_0}\tilde{\underline{D}}(t-t_0)\underline{\Gamma}_{t_0}^{T}\mathbf{k}}, \quad \mathbf{k}(t)\equiv\mathbf{k}\underline{\Gamma}_{t_0}\underline{\Gamma}_t^{-1},
\end{aligned}
\tag{38}
$$

where V is the volume of the scattering region and the above result holds for $t-t_0 \gg 1/\omega$, i.e., time scales much greater than the flow period which permits us to preaverage to get $\tilde{\underline{D}}$. The δ function is defined over the finite volume V [i.e., $\delta(0)=V/(2\pi)^3$]. Note that the average must be taken both over diffusion histories during $[t_0,t]$, i.e., over the Gaussian random force $\mathbf{f}_G$, and also over initial particle positions $\mathbf{R}_G(t_0)$ [namely, $(1/N)\sum_i$]. We have assumed a uniform distribution of particles in space, as is appropriate to the spatially linear incompressible flows we consider (a uniform distribution is unchanged by such flows). Other distributions are of course experimentally accessible. Note that in the solution for $\mathbf{R}_G(t)$, Eq. (8), $\mathbf{R}_G(t_0)$ is a *given* initial condition and the noise $\mathbf{f}_G$ in the integral is assumed to refer to times greater than t_0, i.e., is independent of $\mathbf{R}_G(t_0)$ (thus is one were to discretize time into units of size Δt, the lower limit of the sum would be $t_0+\Delta t$ rather than t_0). Hence we are able to factorize the two averages over $\mathbf{f}_G$ and $\mathbf{R}_G(t_0)$ in Eq. (38). The statistical independence of the N particles in the system and the vanishing of $\langle \exp(i\mathbf{k}\cdot\mathbf{R}_G)\rangle$ for $\mathbf{k}\neq\mathbf{0}$ have also been used. We emphasize the role of the δ function which selects times such that $\underline{\Gamma}_t=\underline{\Gamma}_{t_0}$; consequently the scattering function ends up being exponential in the time difference $t-t_0$. The δ function selects $\mathbf{k}(t)$ which is the wave vector a plane-wave density disturbance, initially of wave vector $\mathbf{k}$, would have after time t if it evolved under the flow alone (i.e., no thermal fluctuations), i.e., according to the deterministic propagator $\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}$. The determinant of this propagator equals unity in our incompressible flows ($\underline{A}$ is traceless).

In the relatively simple extensional and shear cases, Eq. (38) gives, respectively,

$$
S_G(\mathbf{k},t)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t)) \times\exp\left[-\frac{1}{2}\left[\sum_{\alpha=x,y,z}\mathbf{k}_\alpha^2(\underline{\Gamma}_{t_0})_{\alpha\alpha}^2\tilde{\underline{D}}_{\alpha\alpha}\right](t-t_0)\right],
\tag{39}
$$

where the elements $\tilde{\underline{D}}_{xy}$ correspond to the extensional case, Eq. (23), and

$$
S_G(\mathbf{k},t)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))\exp\left\{-\frac{(t-t_0)}{2}\left[\sum_{\alpha=x,y,z}(\mathbf{k}_\alpha)^2\tilde{\underline{D}}_{\alpha\alpha}+\mathbf{k}_x^2\tilde{\underline{D}}_{yy}\left[\lambda\int_0^{\omega t}du\,g(u)\right]^2+2\mathbf{k}_x\mathbf{k}_y\tilde{\underline{D}}_{yy}\lambda\int_0^{\omega t}du\,g(u)\right]\right\},
\tag{40}
$$

where $\tilde{\underline{D}}$ in shear is given by Eq. (35).

Figure 1 illustrates $S_G(\mathbf{k},t)$ for extensional sinusoidal flow and the choice $\mathbf{k}=(k_x,0,0)$ in which case one has from Eq. (39)

$$
S_G(\omega\tau_k,\lambda,\omega(t-t_0),\phi_0)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))\exp\left[-\frac{1}{2}\left[\frac{e^{2\lambda\sin\phi_0}\langle e^{2\lambda\sin u}\rangle_u}{\omega\tau_k}\right]\omega(t-t_0)\right],
\tag{41}
$$

where $\tau_k\equiv 1/(\mathbf{k}\underline{D}\mathbf{k})=\zeta_G/k^2$ is the scattering decay time in the absence of flow [$\tau_k=\zeta_G/\mathbf{k}_x^2$ in Eq. (41)] and ϕ_0 is the initial flow phase $\phi_0\equiv\omega t_0$. We have expressed S_G in terms of the physically relevant dimensionless variables. In Fig. 1, $\omega\tau_k=100$, $\lambda=1$, and the maximum value of $\omega(t-t_0)$ equals 400. Note that for S_G to have the above form one requires $\omega(t-t_0)\gg 1$ since the long-time form for the fluctuation in displacement (coarse-grained dynamics characterized by $\tilde{\underline{D}}$) has been used; thus $\omega\tau_k\gg 1$ is also required, i.e., the width of the decay curve must be

sufficient to allow for many flow cycles. (For a choice of $\mathbf{k}$ such that $\omega\tau_k < 1$ a single flow cycle would be probed for which the long-time forms above would be invalid.) Thus $\mathbf{k}$ must be small enough to probe a scale greater than the distance diffused in one cycle. (Note, however, that the scale probed by a given $\mathbf{k}$ vector is enhanced relative to the no-flow value of order $1/k$; this results from $\mathbf{k}$ vectors being stretched and rotated in the flow.) In Fig. 1(a) the complete scattering function is shown, consisting of a large number of δ functions [each δ function comes with a factor $(2\pi)^3/V$ and so is of finite height] whose peaks trace out a smooth exponentially decaying curve. There are two δ functions per flow cycle at times (n integer) $t-t_0=2n\pi/\omega$ and $t+t_0=(2n+1)\pi/\omega$ which are the two times at which $\underline{\Gamma}_t=\underline{\Gamma}_{t_0}$. The decay rate, modified from the no-flow case, is $1/\bar{\tau}_k$ where $\bar{\tau}_k \equiv 1/(\mathbf{k}\underline{\Gamma}_{t_0}\underline{\tilde{D}}\,\underline{\Gamma}_{t_0}^T\mathbf{k})$ [see Eq. (38)]. Evidently, $\bar{\tau}_k$ depends both on the flow strength parameter λ (exponentially for this extensional case) and on the initial phase; in Fig. 1(b) curves for five different initial phases are shown where, for clarity, only the envelopes are plotted. The dashed curve is the no-flow case ($\lambda=0$) for comparison; note that the effective decay rate is sometimes increased and sometimes decreased by the flow depending on the initial phase value. The initial phase value is just a macroscopic property of the flow and so is under the control of the experimentalist; it simply refers to the reference time against which to compare subsequent light intensities in, say, a photon correlation spectroscopy experi-

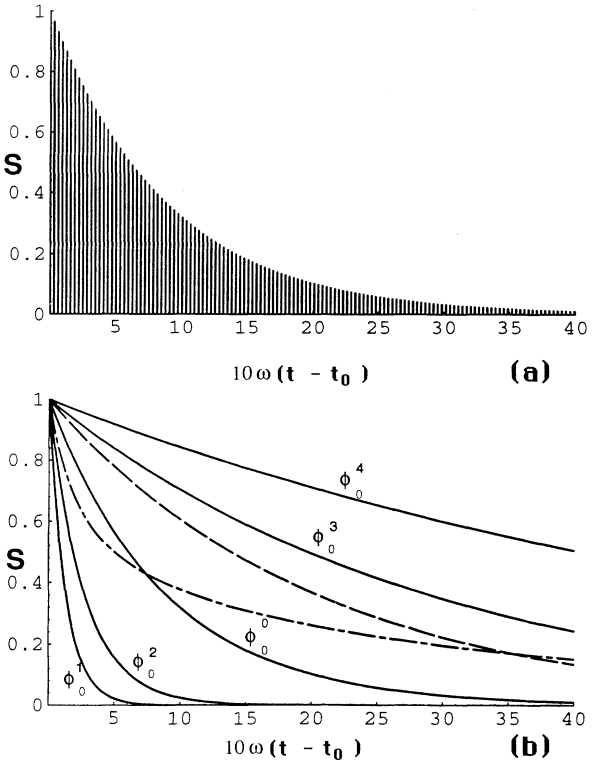

FIG. 1. (a) Center-of-gravity scattering function $S_G(\omega\tau_k,\lambda,\omega(t-t_0),\phi_0)$ vs dimensionless time $\omega(t-t_0)$ in the case of extensional sinusoidal flow [$\Omega(t)=\Omega\cos\omega t$]. Dimensionless parameter values are $\omega\tau_k=100$, $\lambda=1$, $\phi_0=0$, and $\mathbf{k}=(k_x,0,0)$ where the flow matrix $\underline{A}$ is diagonalized in this coordinate system. (b) Solid black curves are the envelopes of center-of-gravity scattering functions as in (a) but for a range of different initial phases ϕ_0: $\phi_0^n=n\pi/5$, $n=0,1,2,3,4$. The dot-dashed curve is the average of these five, and for comparison the scattering function without flow is plotted (dashed curve).

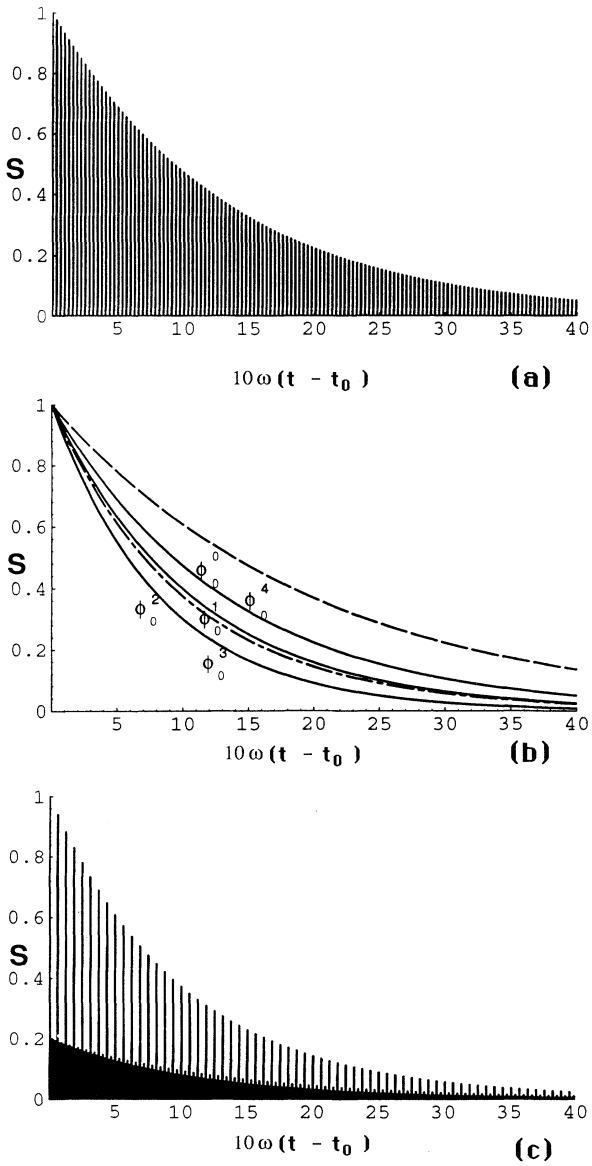

FIG. 2. (a) As Fig. 1(a) but for sinusoidal shear flow [$\Omega(t)=\Omega\cos\omega t$] and $\mathbf{k}=(k_x,0,0)$ where flow is in the x direction. (b) As Fig. 1(b) but for sinusoidal shear flow. (c) Repeat of the dot-dashed curve of (b), but now the complete averaged function is exhibited, including the δ functions. After five initial phase averages the second family of δ functions is reduced in amplitude and spread out. The dot-dashed curve of (b) is the envelope of the taller family.

ment. If that initial phase is kept fixed, the observed curves are of the type shown in Figs. 1(a) and 1(b) (the solid curves). The experimentalist may choose instead to average uniformly over initial phases; also shown in Fig. 1(b) (the dot-dashed curve) is an average over the initial phases represented by the solid curves. This gives another (nonexponentially) decaying curve; averaging over a larger number of initial phases in fact has little effect on this curve. This would be the experimentally observed relation if measurements were taken at random initial times. On average, the flow enhances the decay rate which is essentially the same as the statement that diffusivity is always enhanced.

Figures 2(a) and 2(b) are a repeat of Figs. 1(a) and 1(b) for sinusoidal shear flow, with the same values for the dimensionless parameters and for $\mathbf{k}$:

$$S_G(\omega\tau_k,\lambda,\omega(t-t_0),\phi_0)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))\exp\left[-\frac{1}{2}\left[\frac{1+\lambda^2/2+\lambda^2\sin^2\phi_0}{\omega\tau_k}\right]\omega(t-t_0)\right] . \tag{42}$$

Note that the effect of λ on $\bar{\tau}_k\equiv\tau_k/(1+\lambda^2/2+\lambda^2\sin^2\phi_0)$ is now quadratic rather than exponential. Figure 2(c) is a repeat of the dot-dashed curve in Fig. 2(b), i.e., an average over the initial phases, but now the full structure including δ functions is exhibited. Under averaging only the $t-t_0=2n\pi/\omega$ family of δ functions survives untouched, since their positioning "resonates" with the flow. The $t+t_0=(2n+1)\pi/\omega$ family is further reduced in amplitude after each bout of averaging, being "out of phase" with the flow. In the limit of a continuous average over initial conditions this family disappears altogether, i.e., the total area becomes spread over the entire $t-t_0$ interval.

Enhanced diffusivity effects have been observed and measured in this way by Xia *et al.* [9] who employed forced Rayleigh scattering on a colloidal solution subjected to oscillatory shear flow. They measured $S_G(\mathbf{k},t)$, obtaining a profile of the type illustrated in Fig. 2(a).

An important experimental issue is the extent to which the total time-integrated scattering intensity is reduced by the flow. In the presence of the oscillatory flow, coherent contributions can only occur twice a cycle when the flow brings back a scattering center to within $1/k$ of its original position. Consequently, one anticipates a considerable reduction in intensity. Each δ function, taken with its $(2\pi)^3/V$ factor, is of height unity. The width as a function of its full argument is of order $L^{-1}\equiv V^{-1/3}$ in each Cartesian direction; thus for a given $\mathbf{k}$ the order of magnitude of the width in $t-t_0$ is obtained by equating the change in the argument, for a given change $\Delta(t-t_0)$, to $1/L$: $\Delta\{|\mathbf{k}(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})|\}\sim 1/L$. This change is evaluated by differentiating the argument with respect to time subject to the condition $\underline{\Gamma}_t=\underline{\Gamma}_{t_0}$ which pertains at any peak. Thus one gets $\Delta(t-t_0)\sim 1/(k\Omega L)$ using $d\underline{\Gamma}/dt=\Omega(t)\underline{A}\,\underline{\Gamma}$ and using the fact that the elements of $\underline{A}$ are of order unity. Since there are of order $\omega\bar{\tau}_k$ peaks in total the net area is of order $\bar{\tau}_k/kL\lambda$ which should be compared to the area of order τ_k without flow. The fractional reduction in total intensity is thus of order $1/kL\lambda$ (this reduction is modified by the fact that $\bar{\tau}_k$ differs from τ_k in a t_0-dependent manner, but the $1/kL$ factor is dominant). This is a considerable reduction and complicates experimentation; summing over many initial times t_0 may be required to amass sufficient total intensity.

To conclude this section, let us treat the center-of-gravity displacement for short times compared to the flow period. Consider the case where λ is of order unity. Then the deterministic (i.e., flow only) propagator may be expanded as

$$\begin{aligned}\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}&=\exp\{\underline{A}\int_{t_0}^{t}\Omega\}=\exp\{\underline{A}[\Omega(t_0)(t-t_0)+\tfrac{1}{2}g'(\omega t_0)\Omega\omega(t-t_0)^2+\cdots]\}\\&=1+\underline{A}[\Omega(t_0)(t-t_0)+\tfrac{1}{2}g'(\omega t_0)\Omega\omega(t-t_0)^2]+(\underline{A}^2/2)[\Omega(t-t_0)]^2+\cdots ,\\&\qquad\qquad \Omega(t-t_0),\omega(t-t_0)\ll 1 .\end{aligned} \tag{43}$$

We can use this directly in the deterministic part of Eq. (14), and in the fluctuation part in Eq. (14) one gets from Eq. (11)

$$\begin{aligned}2\underline{D}\int_{t_0}^{t}\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_t\underline{\Gamma}_{t'}^{-1})^T&=2\underline{D}\int_{t_0}^{t}[1+(\underline{A}+\underline{A}^T)\Omega(t_0)(t-t_0)+\cdots]\\&=2\underline{D}(t-t_0)[1+O(\Omega(t-t_0))] .\end{aligned} \tag{44}$$

The total displacement is therefore given by

$$\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle=[\Omega(t_0)(t-t_0)]^2\underline{A}\mathbf{R}_G(t_0)\mathbf{R}_G(t_0)\underline{A}^T+2\underline{D}(t-t_0),\quad \Omega(t-t_0),\omega(t-t_0)\ll 1 . \tag{45}$$

The relative corrections are of order $\Omega(t-t_0),\omega(t-t_0)$. For short times the fluctuations are as without flow to leading order, i.e., the equilibrium diffusivity is recovered. The deterministic part is linear in time (on these time scales the flow gradient is effectively unchanging). Note that the squared displacement is quadratic in the small parameter $\Omega(t-t_0)$; it is of course quite wrong to discard it as a higher-order term since it multiples the "infinite" $\mathbf{R}_G(t_0)$. It will prove interesting in Sec. V to compare the above small-time result with that for the displacement of a polymer chain unit.

III. ENHANCED DIFFUSIVITY: DYNAMICS OF A CHAIN UNIT

We now specialize to a dilute polymer solution. The internal polymer degrees of freedom are excited by the flow field when $\Omega,\omega \gg 1/\tau_0$ where τ_0 is the longest polymer relaxation time. This inequality is assumed throughout this and the following two sections (see Fig. 5). In the following we will see that the rms displacement of one unit of the polymer chain is characterized by an enhanced effective diffusivity in a similar fashion to the center of gravity; however, several important differences arise from the fact that the motion of a monomer, unlike that of a Brownian particle, is influenced by its neighboring monomers. This monomer segment is attached to a polymer chain undergoing periodic deformation.

The Rouse dynamics of our polymer in the flow field $\mathbf{v}(\mathbf{r},t)$ of Eq. (1) are [3]

$$\frac{\partial \mathbf{r}(s,t)}{\partial t}=\frac{1}{\zeta}\frac{\partial^2 \mathbf{r}(s,t)}{\partial s^2}+\Omega g(\omega t)\underline{A}\,\mathbf{r}(s,t)+\mathbf{f}(s,t)\ , \tag{46}$$

where $\{\mathbf{r}(s,t)\}_{s=0}^{s=N}$ denotes the conformation at time t of a chain of N units, $1/\zeta$ is the monomer mobility, and the correlation of the Gaussian random force of zero mean is

$$\langle \mathbf{f}(s,t)\mathbf{f}(s',t')\rangle=\frac{2}{\zeta}\underline{I}\delta(s-s')\delta(t-t')\ . \tag{47}$$

Equation (46) is solved with free end boundary conditions, i.e., $\partial \mathbf{r}(s,t)/\partial s=0$ at $s=0$ and N. We define the displacement vector of the sth chain unit during the interval $[t_0,t]$ to be $\mathbf{d}(s,t_0,t)\equiv\mathbf{r}(s,t)-\mathbf{r}(s,t_0)$. Our objective in this section is to calculate the basic correlation function characterizing the statistics of $\mathbf{d}(s,t_0,t)$. $\mathbf{d}(s,t_0,t)$ can be expressed in terms of the Rouse modes

$$\mathbf{r}_p(t)\equiv\sqrt{2/N}\int_0^N ds\ \mathbf{r}(s,t)\cos\frac{p\pi s}{N},\quad p=0,1,2,3,\ldots \tag{48}$$

as

$$\mathbf{d}(s,t_0,t)=[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]+[\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]\ , \tag{49}$$

where $\mathbf{R}_G(t)\equiv(1/N)\int_0^N ds'r(s',t)=(1/\sqrt{2N})\mathbf{r}_0(t)$ is the center of gravity of the polymer, and $\mathbf{u}(s,t)$ is the position of the sth chain unit relative to the center of gravity,

$$\mathbf{u}(s,t)\equiv\sqrt{2/N}\sum_{p=1}^{\infty}\mathbf{r}_p(t)\cos\left[\frac{p\pi s}{N}\right]\ . \tag{50}$$

Integrating Eq. (46) with respect to s from $s=0$ to $s=N$, and using the free end boundary conditions and Eq. (47), one establishes immediately that $\mathbf{R}_G$ obeys the dynamics studied in Sec. II, Eq. (6), with random force correlations given by Eq. (7) provided one identifies $\zeta_G\equiv N\zeta$ (the standard result [19]). Thus we are already equipped with a full understanding of the behavior of the zeroth mode. The behavior of the internal modes, $q\neq 0$, which are the basis for $\mathbf{u}(s,t)$, is qualitatively different. From Eq. (46) their dynamics are

$$\dot{\mathbf{r}}_p=-\frac{\mathbf{r}_p}{\tau_p}+\Omega(t)\underline{A}\,\mathbf{r}_p+\mathbf{f}_p\ , \tag{51}$$

where the random force correlations are

$$\langle \mathbf{f}_p(t)\mathbf{f}_{p'}(t')\rangle=\frac{2}{\zeta}\underline{I}\delta_{p,p'}\delta(t-t') \tag{52}$$

and $\tau_p\equiv\zeta N^2/\pi^2p^2$ is the mode relaxation time. Equation (52) together with the linearity of the mode dynamics, Eq. (51), implies that the modes are statistically independent of one another (which is of course the essence of the Rouse model and is unspoiled by our linear flow field). Thus from Eq. (49) the correlation function of the displacement may be expressed as

$$\begin{aligned}\langle \mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle&=\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle+\langle[\mathbf{u}(s,t)-\mathbf{u}(s,t_0)][\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]\rangle\\&=\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle\\&\quad+\left[\frac{2}{N}\right]\sum_{p=1}^{\infty}\cos^2\left[\frac{p\pi s}{N}\right]\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle\ .\end{aligned} \tag{53}$$

Evidently the correlation function we seek is determined by the mode displacement correlation function $\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle$ whose evaluation we now address. Begin by defining [3] $\mathbf{r}_p(t)\equiv\underline{\Gamma}_t\mathbf{x}_p(t)$; the motivation is to factor out the deterministic part of the mode evolution. From Eq. (51) the dynamics of $\mathbf{x}_p$ are easily obtained:

$$\dot{\mathbf{x}}_p=-\frac{\mathbf{x}_p}{\tau_p}+\underline{\Gamma}_t^{-1}f_p\ . \tag{54}$$

These are the dynamics of an oscillator, of natural frequency τ_p, additively perturbed by a random force multiplying an "envelope" of period $2\pi/\omega$. When this period is very small compared to τ_p the oscillator is unable to

respond to the systematic part of the time dependence of $\underline{\Gamma}_t^{-1} f_p$ and is affected by only the time average, i.e., a new effective δ-correlated random force when coarse grained over the time scale $1/\omega$. In order to explicitly demonstrate this, we first solve Eq. (54) for large times (relative to the instant at which the flow is "switched on"),

$$\mathbf{x}_p(t) = \int_{-\infty}^{t} dt' e^{-(t-t')/\tau_p} \underline{\Gamma}_{t'}^{-1} f_p(t') \ . \tag{55}$$

Note that any initial state is forgotten after a time of order τ_p, in contrast to the zeroth mode for which keeping track of the initial condition was essential [see Eq. (8)]. The $\mathbf{x}_p$ correlation function is thus

$$\langle \mathbf{x}_p(t)\mathbf{x}_q(t_0)\rangle = \delta_{p,q} e^{-(t-t_0)/\tau_p} \frac{2}{\zeta} \times \int_{-\infty}^{t_0} dt' e^{-2(t_0-t')/\tau_p} \underline{\Gamma}_{t'}^{-1} (\underline{\Gamma}_{t'}^{-1})^T \ , \tag{56}$$

where the random force correlation Eq. (52) was used. For those modes such that $\tau_p \gg 1/\omega$, the exponential factor in the integrand in Eq. (56) decays much more slowly than the $\underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_{t'}^{-1})^T$ factor which can thus to a good approximation be replaced by its time average. Using Eq. (13) this leads to

$$\begin{aligned} \langle \mathbf{x}_p(t)\mathbf{x}_p(t_0)\rangle &\approx \langle \underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_{t'}^{-1})^T\rangle_{t'} \frac{\tau_p}{\zeta} e^{-(t-t_0)/\tau_p} \\ &= \underline{E} \frac{\tau_p}{\zeta} e^{-(t-t_0)/\tau_p} \ , \\ \langle \mathbf{r}_p(t)\mathbf{r}_p(t_0)\rangle &\approx \underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_{t_0}^T \frac{\tau_p}{\zeta} e^{-(t-t_0)/\tau_p}, \quad p \ll p_\omega \ . \end{aligned} \tag{57}$$

Here $\underline{E}$ is the enhancement matrix which characterized the center-of-gravity flow dynamics and

$$\begin{aligned} &\omega\tau_{p_\omega} \equiv 1 \ , \\ &p_\omega \approx (\omega\tau_0)^{1/2} \ , \end{aligned} \tag{58}$$

where τ_0 is the longest relaxation time of the Rouse chain. The mode $p = p_\omega$ is that mode whose relaxation time just matches the period of the flow. It defines the "ω blob" of Ref. [3], namely, a collection of $s_\omega \sim N/p_\omega$ chain units whose relaxation time equals ω^{-1}. Portions of the polymer which are large compared to this blob deform *affinely* in the flow without slip as if they were passive fluid elements, their relaxation rates being too small to respond to the changing field (see Fig. 5). Correspondingly, small p modes relative to p_ω also deform affinely; Eq. (57) exhibits an affine form since $\mathbf{y}_t\mathbf{y}_t = \underline{\Gamma}_t\{\mathbf{y}_0\mathbf{y}_0\}\underline{\Gamma}_t^T$ is the evolution of a fluid element $\mathbf{y}_t$ in the pure velocity-gradient field, i.e., $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_t$ is the affine operator. This operator acts on an enhanced "reference" fluctuation in the mode extension as represented by the mode dyad taken at times equal to integral multiples of the flow period when $\langle \mathbf{rr}\rangle = \underline{E}(\tau_p/\zeta)$. This enhancement is the long-time effect of the flow.

Now recall that the original specification of the flow gradient field included the vanishing of its time average [see Eq. (3)]. This was required in order that the center of gravity $\underline{\tilde{D}}$ exist. The derivation of Eq. (57) in fact remains valid provided this time average is less the Rouse chain relaxation frequency $1/\tau_0$ (a somewhat milder restriction). If this condition were not to be satisfied, then there would exist $p < p_\omega$ modes such that $\Omega > \tau_p^{-1}$. For such modes the integrand in Eq. (56) would, in the case of a "generic" flow matrix $\underline{A}$ with a nonzero symmetric part (see Appendix A), suffer net exponential growth in time (the exponential mode decay being insufficient to beat the exponential flow growth multiplying its oscillatory part) and the $\langle \mathbf{xx}\rangle$ correlation function would not exist. Physically this means that such modes "run away," i.e., continue to grow without bound as does the chain size [3]. A small (relative to $1/\tau_0$) but finite time average yields small corrections to Eq. (57). In the special case where the eigenvalues of $\underline{A}$ all vanish (case 1 in Appendix A) the correlation function still exists since the effect of the flow terms in the integrand in Eq. (56) is not exponential but polynomial. Thus the exponential mode decay still wins. Shear flow is an important example of this type.

The x_p correlation function for small p, Eq. (57), is of the form of the correlation function for the pth Rouse mode *in the absence of flow,* namely, $(\tau_p/\zeta)\exp\{-(t-t_0)/\tau_p\}$, but with an *enhanced* and tensorial fluctuation. Just as the fluctuations in the center-of-gravity displacement are enhanced by the flow, $\underline{D} \to \underline{\tilde{D}}$, so the mode fluctuations are identically enhanced by the "factor" $\underline{E}$. As for the center of gravity the flow induces inequality in the diagonal elements of the fluctuation tensor as well as off-diagonal correlations.

It is instructive to compare the fluctuation in center-of-gravity displacement, $2\underline{\Gamma}_t\{\underline{\tilde{D}}(t-t_0)\}\underline{\Gamma}_t^T$, Eq. (16), with the mode correlation which from Eq. (57) is given by $\langle r_p(t)r_p(t_0)\rangle = \underline{\Gamma}_t\{N\underline{\tilde{D}}\tau_p \exp[-(t-t_0)/\tau_p]\}\underline{\Gamma}_{t_0}^T$. The operator $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_t^T$ appears in the former, $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_{t_0}^T$ in the latter. The center of gravity loses all memory of the state of the flow at t_0; on the contrary, a mode never loses such memory. This derives from the fact that the steady-state distribution for each mode is time dependent (periodic) so that any correlation relative to the state of the mode at some reference time t_0 depends on the state of the flow at that time.

The essence of the flow problem is the time dependence induced in the probability distribution for $\mathbf{r}_p(t)$; we have now established that the dynamics of $\mathbf{x}_p(t)$ (for small p) are the underlying *stationary* process. According to Eq. (57) the mean-square amplitude (and indeed the probability distribution) is independent of time and the two-time correlation depends only on the difference, i.e., time translational invariance is recovered for this process. Moreover, Eq. (57) implies that $\langle \mathbf{x}_p(t)\mathbf{x}_p(t_0)\rangle$ is a *symmetric* matrix [since $\underline{\tilde{D}}$ is symmetric—see comments following Eq. (15)], i.e., the properties of a reversible process are recovered. These essential properties of the statistics of $\mathbf{x}_p$ enable us to express the desired mode displacement correlation function in the most rational manner as follows. First we separate out the *deterministic* part of the evolution of $\mathbf{r}_p$, which is given by (recall that $\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}$ is the deterministic propagator)

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\det}=\langle(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{r}_p(t_0)(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-\underline{I})\mathbf{r}_p(t_0)\rangle$$
$$=(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\langle\mathbf{x}_p(t_0)\mathbf{x}_p(t_0)\rangle(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T . \tag{59}$$

Thus

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle=\langle[\underline{\Gamma}_t\mathbf{x}_p(t)-\underline{\Gamma}_{t_0}\mathbf{x}_p(t_0)][\mathbf{x}_p(t)\underline{\Gamma}_t^T-\mathbf{x}_p(t_0)\underline{\Gamma}_{t_0}^T]\rangle$$
$$=(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T$$
$$+\underline{\Gamma}_t\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle\underline{\Gamma}_{t_0}^T+\underline{\Gamma}_{t_0}\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle\underline{\Gamma}_t^T$$
$$-\underline{\Gamma}_t\langle\mathbf{x}_p(t)\mathbf{x}_p(t_0)\rangle\underline{\Gamma}_{t_0}^T-\underline{\Gamma}_{t_0}\langle\mathbf{x}_p(t_0)\mathbf{x}_p(t)\rangle\underline{\Gamma}_t^T,\quad p<p_\omega , \tag{60}$$

where we have added and subtracted the deterministic part, Eq. (59), and the time independence of $\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle$ has led to the cancellation of four terms above. Using the symmetricity property $\langle\mathbf{x}_p(t)\mathbf{x}_p(t_0)\rangle=\langle\mathbf{x}_p(t_0)\mathbf{x}_p(t)\rangle$ we have

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle=(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T$$
$$+\tfrac{1}{2}\{\underline{\Gamma}_t\langle[\mathbf{x}_p(t)-\mathbf{x}_p(t_0)][\mathbf{x}_p(t)-\mathbf{x}_p(t_0)]\rangle\underline{\Gamma}_{t_0}^T\}$$
$$+\tfrac{1}{2}\{\underline{\Gamma}_t\langle[\mathbf{x}_p(t)-\mathbf{x}_p(t_0)][\mathbf{x}_p(t)-\mathbf{x}_p(t_0)]\rangle\underline{\Gamma}_{t_0}^T\}^T,\quad p<p_\omega . \tag{61}$$

This is the desired form best elucidating the various physical effects for small p modes. In Appendix B it is demonstrated that for long times those modes corresponding to scales within the "ω blob," i.e., $p>p_\omega$, have negligible effect on the chain unit displacement $d(s,t_0,t)$; that is, we may use the above small p form in Eq. (53) as if it were appropriate to *all* p, to within a small correction factor of order $[\omega(t-t_0)]^{-1/2}$. Now all terms in Eq. (61) are quadratic in $\mathbf{x}_p$ and so, via Eq. (57), are equal to the corresponding expressions for a Rouse mode *without flow* (for which $\underline{E}$ is replaced by $\underline{I}$) multiplied by the "enhancement operator" $\underline{E}$. Therefore on substituting the first term on the right-hand side of Eq. (61) into Eq. (53), the $\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle$ part will yield $\underline{E}$ operating on the *equilibrium* value of $\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle$, as may be seen by squaring $\mathbf{u}$ in Eq. (50). Similarly, the $\langle[\mathbf{x}_p(t)-\mathbf{x}_p(t_0)][\mathbf{x}_p(t)-\mathbf{x}_p(t_0)]\rangle$ factors in Eq. (61) will yield $\tilde{\underline{D}}\zeta_G$ operating on the *equilibrium* value of the displacement correlation function for a chain unit (the center-of-gravity motion subtracted off). Thus for large times $t-t_0\gg\omega^{-1}$ we have

$$\langle\mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle=\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle+(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\underline{E}\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle^{\mathrm{eq}}(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T$$
$$+[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S\langle[\mathbf{u}(s,t)-\mathbf{u}(s,t_0)][\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]\rangle^{\mathrm{eq}} , \tag{62}$$

where superscript S denotes the symmetric part. $\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle^{\mathrm{eq}}$ denotes the well-known equilibrium (no flow) correlation of the position of the sth unit relative to the center of gravity:

$$\langle\mathbf{u}(s,t)\mathbf{u}(s,t)\rangle^{\mathrm{eq}}=\frac{2}{N}\sum_{p=1}^{p=\infty}\cos^2\left[\frac{p\pi s}{N}\right]\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle^{\mathrm{eq}}$$
$$=N\left[\left[\frac{s}{N}\right]^2-\left[\frac{s}{N}\right]+\frac{1}{3}\right]\underline{I} . \tag{63}$$

We have used $\langle\mathbf{xx}\rangle^{\mathrm{eq}}=N\underline{D}\tau_p=N(\underline{I}/\zeta_G)(\zeta N^2/\pi^2p^2)=\underline{I}N^2/\pi^2p^2$ and the identity $\sum_{p=1}^{p=\infty}(1/p^2)\cos^2(p\pi s/N)=(\pi^2/2)[(s/N)^2-(s/N)+\frac{1}{3}]$. The equilibrium u displacement correlation function is

$$\langle[\mathbf{u}(s,t)-\mathbf{u}(s,t_0)][\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]\rangle^{\mathrm{eq}}=\frac{4}{N}\sum_{p=1}^{p=\infty}\cos^2\left[\frac{p\pi s}{N}\right]\langle\mathbf{x}_p(t)\mathbf{x}_p(t)\rangle^{\mathrm{eq}}(1-e^{-(t-t_0)/\tau_p})$$
$$=\frac{4N}{\pi^2}\sum_{p=1}^{p=\infty}\cos^2\left[\frac{p\pi s}{N}\right]\frac{1}{p^2}(1-e^{-(t-t_0)/\tau_p})\underline{I} . \tag{64}$$

For short times (relative to the relaxation time of the section of polymer joining the sth segment to the nearest chain end) the sum can be approximated by an integral and gives the well-known $(t-t_0)^{1/2}$ dependence for the mean-square displacement [18]. For such small times then our final result reads

$$\langle \mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle = \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle + (\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\underline{E}(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T\left\{N\left[\left[\frac{s}{N}\right]^2-\left[\frac{s}{N}\right]+\frac{1}{3}\right]\right\} + [\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S\left\{C\left[\frac{t-t_0}{\zeta}\right]^{1/2}\right\}, \quad \omega^{-1}\ll t-t_0\ll\tau_0\ , \tag{65}$$

where $\tau_0\equiv\zeta N^2/\pi^2$ is the longest relaxation time of the Rouse chain and C is a constant equal to $2/(\pi)^{1/2}$ for an inner unit and twice this value for end units, $s=0$ or N.

The physics of the time development of the displacement of a chain unit is now very clear from Eq. (65). The curly brackets in the second and third terms enclose equilibrium (no-flow) quantities. In the second term the equilibrium quantity is operated on by the "enhancement operator" $\underline{E}$, giving the $t=0$ correlation of the position of the sth chain unit relative to the center of gravity. In steady state this latter quantity is expanded by the flow. The outer $\underline{\Gamma}_t-\underline{\Gamma}_{t_0}$ operators represent the effect of the flow as it varies over one period; the expanded chain at $t=0$ suffers *affine* periodic deformation. The physics of this term is rather like that of an elastic band; the time-averaged size of the band is enhanced by the flow, and in addition the band is periodically elongated and compressed in the continuing flow field. This term then corresponds to the motion of the material element at a position s on the band in the frame of reference embedded in the center of gravity of the band. Notice that in the absence of flow this term disappears entirely.

The last term in Eq. (65) describes the effect of certain fluctuations missing from the "elastic band" picture and embodies what we mean by the short-time enhanced diffusivity of a monomer. Now the length of the elastic band represents (enhanced and periodic) spatial fluctuations in the configuration of the entire polymer, i.e., a property of the instantaneous chain probability distribution; the flow enhances the length of the band relative to the no-flow length (equilibrium rms size of the polymer) and moreover modulates it periodically. In contrast this last term describes a fluctuation in the position of a unit relative to its initial position which *continues to grow in time* beyond a scale ω^{-1}. The no-flow displacement in the curly brackets is enhanced by the same tensorial factor as in the previous term. The outer operators again effect the continuing deformation of the flow. Noticeable is the fact that the initial time t_0 is never forgotten by this correlation function; the fluctuation in the displacement of a chain unit depends both on the fluctuation in the destination position (at t) and in the initial position (at t_0). These depend on the state of the chain at the times t and t_0, respectively, i.e., on the fluctuations in monomer positions at those times. This state is periodic.

Define this growing fluctuation term to be $\underline{T}C[(t-t_0)/\zeta]^{1/2}$, where $\underline{T}\equiv\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T$, such that $\underline{T}=\underline{I}$ without flow. Then in the specific case of sinusoidal elongational flow Eq. (33) implies that $\underline{T}_{xx}=\exp\{\lambda(\sin\omega t-\sin\omega t_0)\}\langle\exp\{-2\lambda\sin u\}\rangle_u$. For sinusoidal shear [see Eq. (36)] $\underline{T}_{xy}=\underline{T}_{yx}=(\lambda^2/2)(\sin\omega t+\sin\omega t_0)$, $\underline{T}_{xx}=1+\lambda^2(1/2+\sin\omega t\sin\omega t_0)$, $\underline{T}_{yy}=\underline{T}_{zz}=1$, and all other elements vanish.

In summary, the diffusion of a single chain unit (and the size of the chain as we will see in the next section) are enhanced by the same factor as that for the center of gravity studied in the preceding section where it was demonstrated that $\mathrm{tr}\underline{\tilde{D}}$ exceeds its no-flow value. Thus we may conclude that the rms distance diffused by a chain unit (and the rms size of the polymer chain) are greater in the presence of a periodic flow. The large-time-scale ($t-t_0>1/\omega$) and large-length-scale (compared to the ω blob size) behavior is characterized by pseudoequilibrium forms. Large polymer scales move affinely with the flow and (see Ref. [3] and Sec. III) are characterized by random walk statistics just as in equilibrium, albeit with an enhanced step length and cross correlations between components of each step. The diffusive fluctuations superimposed on this affine deterministic motion grow for large times just as in equilibrium, albeit with an enhanced diffusivity. The enhancements of step length and diffusivity are identical.

IV. POLYMER SCATTERING FUNCTIONS

The dynamical effects described in the preceding section are accessible in scattering experiments on dilute flowing polymer solutions. In this section the measured scattering functions are calculated, assuming sufficient dilution that different polymer chains sum identical contributions incoherently. The total signal therefore equals the number of chains in the scattering region times the single chain scattering function.

In an incoherent experiment, a single monomer per chain is labeled:

$$S_{\mathrm{incoh}}(\mathbf{k},t)\equiv\langle e^{i\mathbf{k}\cdot[\mathbf{r}(s,t)-\mathbf{r}(s,t_0)]}\rangle\ . \tag{66}$$

Splitting r into its center-of-gravity and internal mode parts as before, $r\equiv R_G+u$, one obtains

$$S_{\mathrm{incoh}}(\mathbf{k},t)=\langle e^{i\mathbf{k}\cdot[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)+\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]}\rangle = \langle e^{i\mathbf{k}\cdot[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\cdot\mathbf{k}}\rangle e^{-(1/2)\mathbf{k}\cdot\langle[\mathbf{u}(s,t)-\mathbf{u}(s,t_0)][\mathbf{u}(s,t)-\mathbf{u}(s,t_0)]\rangle\cdot\mathbf{k}}\ . \tag{67}$$

The center-of-gravity average factorizes off (being statistically independent of all other modes, which span u) and we must average both over random force histories and initial values $R_G(t_0)$. This factor is of course just S_G of Sec. II [see Eq. (38)]. The u average (in which we have used the fact that u is Gaussian) involves no initial condition averaging since internal modes lose memory of their initial state in a finite time. To see internal dynamical effects requires time scales far less than the Rouse time, $t-t_0 \ll \tau_0$, when the small-time displacement form, Eq. (65), applies:

$$S_{\text{incoh}}(\mathbf{k},t)=S_G(\mathbf{k},t)\exp\left\{-\frac{1}{2}\mathbf{k}(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})\underline{E}(\underline{\Gamma}_t-\underline{\Gamma}_{t_0})^T N\left[\frac{s}{N}\left[\frac{s}{N}-1\right]+\frac{1}{3}\right]\mathbf{k}\right\} e^{-(1/2)\mathbf{k}[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^s\mathbf{k}\{C[(t-t_0)/\zeta]^{1/2}\}} . \quad (68)$$

Consider the above expression when the flow is switched off. Then the prefactor $S_G(\mathbf{k},t)$ decays on a time scale $\tau_k=N\zeta/k^2\approx\tau_0/(kR_0)^2$ and the second internal mode factor in a time $\tau_k^{\text{pol}}=\zeta/k^4\approx\tau_0/(kR_0)^4$ where $R_0\equiv(3N)^{1/2}$ is the rms polymer size and $\tau_0\approx\zeta R_0^4$ the longest polymer relaxation time. Thus one has $\tau_k^{\text{pol}}/\tau_k\approx(kR_0)^{-2}$. But to see features of the internal dynamics factor requires $t-t_0\approx\tau_k^{\text{pol}}$ which dictates a choice of $\mathbf{k}$ such that $\tau_k^{\text{pol}}\ll\tau_0$ if Eq. (68) is to apply, i.e., $(kR_0)\gg1$. Thus $(t-t_0)/\tau_k\approx\tau_k^{\text{pol}}/\tau_k=(kR_0)^{-2}\ll1$, so the S_G prefactor is very close to unity. Provided one substitutes enhanced versions of the time scales τ_k and τ_k^{pol} the above argument is unmodified when flow is switched on (with λ of order unity the conclusions are essentially unchanged) but now the argument applies to the *envelope* traced out by the δ-function peaks of S_G, i.e., the conclusion is that this envelope is approximately constant. Even on these short-time scales, S_G now plays a crucial role in sharp contrast to the no-flow case, multiplying S_{incoh} by a series of δ functions selecting times t such that $\underline{\Gamma}_t=\underline{\Gamma}_{t_0}$. The effect on the expression in Eq. (68) is that the deterministic "elastic band" part of the exponent is entirely lost:

$$S_{\text{incoh}}(\mathbf{k},t)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))e^{-C[(t-t_0)/\tilde{\tau}_k^{\text{pol}}]^{1/2}} , \quad (69)$$

where the decay rate $1/\tilde{\tau}_k^{\text{pol}}$ is "enhanced" by the flow, relative to the no-flow rate $1/\tau_k^{\text{pol}}$, by a factor $[\hat{\mathbf{k}}\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T\hat{\mathbf{k}}]^2$ (where $\hat{\mathbf{k}}\equiv\mathbf{k}/|\mathbf{k}|$):

$$\frac{1}{\tilde{\tau}_k^{\text{pol}}}\equiv\frac{1}{\zeta}\{\mathbf{k}[\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T]\mathbf{k}\}^2=\frac{1}{\tau_k^{\text{pol}}}[\hat{\mathbf{k}}\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T\hat{\mathbf{k}}]^2 . \quad (70)$$

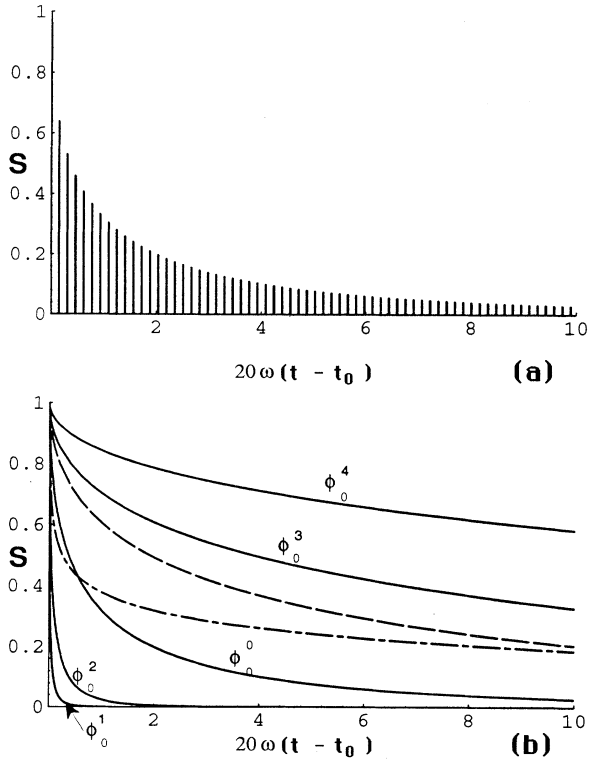

FIG. 3. (a) Incoherent polymer scattering function $S_{\text{incoh}}(\omega\tau_k^{\text{pol}},\lambda,\omega(t-t_0),\phi_0)$ in sinusoidal extensional flow with $\omega\tau_k^{\text{pol}}=20$, $\lambda=1$, $\phi_0=0$, and $\mathbf{k}=(k_x,0,0)$ where the flow matrix A is diagonalized in this coordinate system. (b) As Fig. 1(b) but for the polymer scattering functions with $\omega\tau_k^{\text{pol}}=20$ and $\lambda=1$ as in (a).

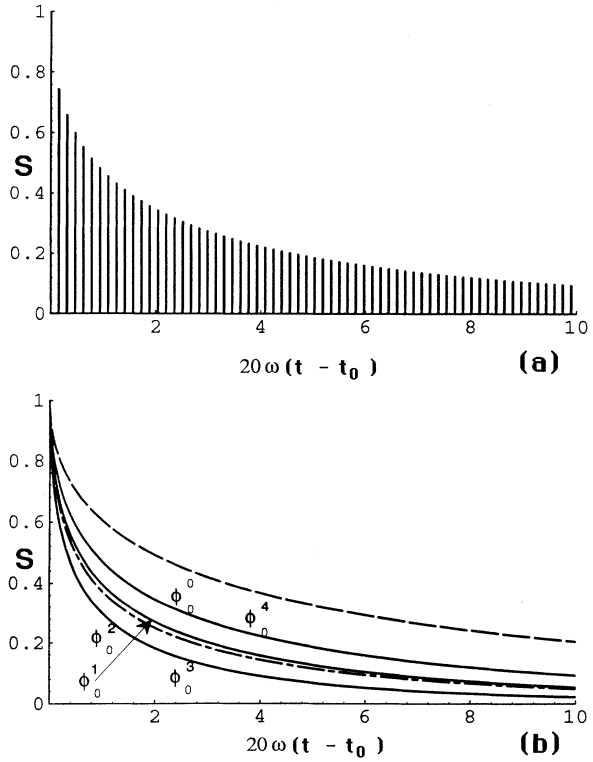

FIG. 4. (a) As Fig. 3(a) but for sinusoidal shear flow and $\mathbf{k}=(k_x,0,0)$ where flow is in the x direction. (b) As Fig. 3(b) but for sinusoidal shear flow.

Figures 3 and 4 depict S_{incoh} for the same flows as Figs. 1 and 2, respectively, for the center of gravity. The relevant parameter values are $\omega\tau_k^{\text{pol}}=20$ and $\lambda=1$. As for the center of gravity, the form in Eq. (69) is valid only on time scales large compared to the flow period, i.e., $\omega\tau_k^{\text{pol}}\gg 1$. Similar remarks as in the case of the S_G curves apply here, with the important difference that the decay is now the exponential of a square root of the time difference.

Next we consider experiments in which every chain unit is labeled, in which case the coherent scattering function is measured:

$$S_{\text{coh}}(\mathbf{k},t)\equiv\left\langle\sum_{s,s'}e^{i\mathbf{k}\cdot[\mathbf{r}(s+s',t)-\mathbf{r}(s',t_0)]}\right\rangle$$
$$=S_G(\mathbf{k},t)\sum_{s,s'}e^{-(1/2)\mathbf{k}\cdot\langle[\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)][\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)]\rangle\cdot\mathbf{k}}\ . \tag{71}$$

The dyad in the exponent is conveniently expressed in terms of the Fourier modes $\{\mathbf{r}_p\}$ as

$$\langle[\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)][\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)]\rangle$$
$$=\frac{2}{N}\sum_{p=1}^{\infty}\left\langle\left[\mathbf{r}_p(t)\cos\frac{p\pi(s+s')}{N}-\mathbf{r}_p(t_0)\cos\frac{p\pi s'}{N}\right]\left[\mathbf{r}_p(t)\cos\frac{p\pi(s+s')}{N}-\mathbf{r}_p(t_0)\cos\frac{p\pi s'}{N}\right]\right\rangle, \tag{72}$$

where the mutual independence of the modes was used. We demonstrate in Appendix B that when $t-t_0\gg\omega^{-1}$, $s\gg s_\omega$ all modes may be replaced with the small p affine form [$\mathbf{r}_p=\underline{\Gamma}_t\mathbf{x}_p$ with $\mathbf{x}_p$ given by Eq. (57)] with small corrections. Approximating thus and exploiting the equilibrium nature of the $\mathbf{x}_p$ dynamics [namely, the time translational invariance and symmetry properties of the $\langle\mathbf{x}_p(t)\mathbf{x}_p(t_0)\rangle$ correlation function as discussed in Sec. II] one obtains

$$\langle[\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)][\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)]\rangle$$
$$=2\sum_{p=1}^{\infty}\left[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T\left\{\frac{\tau_p}{\zeta}\right\}\cos^2\frac{p\pi(s+s')}{N}+\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T\left\{\frac{\tau_p}{\zeta}\right\}\cos^2\frac{p\pi s'}{N}\right.$$
$$\left.-\{\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T+\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_t^T\}\left\{\frac{\tau_p}{\zeta}\right\}\cos\frac{p\pi(s+s')}{N}\cos\frac{p\pi s'}{N}\right]e^{-(t-t_0)/\tau_p}$$
$$\xrightarrow{\underline{\Gamma}_t=\underline{\Gamma}_{t_0}}2\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T\sum_{p=1}^{\infty}\left\{\frac{\tau_p}{\zeta}\right\}\left[\left[\cos\frac{p\pi(s+s')}{N}-\cos\frac{p\pi s'}{N}\right]^2+2\cos\frac{p\pi(s+s')}{N}\cos\frac{p\pi s'}{N}\{1-e^{-(t-t_0)/\tau_p}\}\right]. \tag{73}$$

The last expression in Eq. (73) is the form of the correlation function at the relevant times which are dictated by the δ functions of S_G. This expression is simply $\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T$ operating on the no-flow value which was first evaluated by de Gennes [48]. Evidently the first term in the no-flow part is the equilibrium mean-square separation between chain units (distant s from one another along the backbone) and equals s. Considering times $t-t_0\ll\tau_0$ we thus have

$$\langle[\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)][\mathbf{u}(s+s',t)-\mathbf{u}(s',t_0)]\rangle_{\underline{\Gamma}_t=\underline{\Gamma}_{t_0}}=\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T\left\{|s|+\frac{2}{\sqrt{\pi}}\left[\frac{t-t_0}{\zeta}\right]^{1/2}g\left[\frac{s^2\zeta}{4(t-t_0)}\right]\right\}, \tag{74}$$

where the curly brackets enclose de Gennes' equilibrium expression in which [48] g is a dimensionless function of the dimensionless parameter $s^2\zeta/(t-t_0)$ and $g(u)\equiv\int_1^\infty dx\,e^{-ux^2}/x^2$ such that $g(0)=1$ and $g(\infty)=0$. (The parameters W and σ in de Gennes' formulas are identified as $W=1/\zeta$ and $\sigma^2=3$.) Note that two limits are correctly recovered. First, when $s=0$ one obtains the chain unit displacement correlation function Eq. (65) evaluated at $\underline{\Gamma}_t=\underline{\Gamma}_{t_0}$ and with the constant C as appropriate to an internal chain unit (when we integrate below over all units the chain ends will have negligible weighting for large N). Secondly, when $t=t_0$ the expression yields the steady-state equal time separation between two chain units separated by s along the backbone as calculated in Ref. [3]. This latter quantity is just (one-third of) the equilibrium separation s multiplying the flow operator $\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T$. Since the correlation function decays as a function of s on a scale far less than N, we can express the sum in Eq. (71) as an integral, $\sum_s\sum_{s'}\to 2N\int_0^\infty ds$, where s denotes a positive separation between two chain units. Changing the integration variable to $v\equiv s\{\zeta/[4(t-t_0)]\}^{1/2}$ one obtains

$$S_{\text{coh}}(\mathbf{k},t)=\frac{(2\pi)^3}{V}\delta(\mathbf{k}-\mathbf{k}(t))S_{\text{coh}}(\mathbf{k},t_0,t_0)\theta$$
$$\times\int_0^\infty dv\,e^{-\theta\{v+(1/\sqrt{\pi})g(v^2)\}}\ , \tag{75}$$

where

$$\theta \equiv \left[\frac{4(t-t_0)}{\zeta}\right]^{1/2} \frac{1}{2}\mathbf{k}[\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T]\mathbf{k} = \left[\frac{t-t_0}{\bar{\tau}_k^{\rm pol}}\right]^{1/2}, \quad (76)$$

and the equal time coherent scattering function is

$$S_{\rm coh}(\mathbf{k},t_0,t_0) = \frac{4N}{\mathbf{k}[\underline{\Gamma}_{t_0}\underline{E}\,\underline{\Gamma}_{t_0}^T]\mathbf{k}} . \quad (77)$$

The final expression is identical to the corresponding expression without flow, with two important modifications. Analogously to the no-flow expression, $S_{\rm coh}(\mathbf{k},t)/S_{\rm coh}(\mathbf{k},t_0,t_0)$ depends on $\mathbf{k}$ via only a single parameter, namely, θ. However, the flow significantly modifies the form of θ which now depends on the enhancement tensor $\underline{E}$ and the initial time of observation t_0; τ_k is replaced by $\bar{\tau}_k^{\rm pol}$, Eq. (70). As for the coherent case, the flow also fractures the smooth curve into a set of δ functions whose envelope is smooth.

The equal time scattering function, Eq. (77), is the Fourier transform of the chain density at t_0 and thus directly reflects the instantaneous chain conformation. Let us use Eq. (74) to obtain an expression for the most basic conformational property, the mean size of a polymer segment comprising s units. When $s \gg s_\omega$, we can use Eq. (74) in the special case $t=t_0$. Calling the spatial separation between two chain units $\mathbf{R}(s,t) \equiv \mathbf{u}(s+s',t) - \mathbf{u}(s',t)$, we have $(s>0)$

$$\langle \mathbf{R}(s,t)\mathbf{R}(s,t)\rangle = \underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T s , \quad (78)$$

where s' is taken far from chain ends (and so drops out) and we have used $g(\infty)=0$ in Eq. (74). This is the generalization to arbitrary flow of the derivation in Ref. [3] of the trace of the above quantity in the cases of shear and extensional flow. It describes *affine* deformation of the polymer chain in the flow, i.e., a time variation which is the same as that of a fluid element. As anticipated at the end of the preceding section, the size of a blob of s units is the random walk result but with an enhancement factor. At $t=0$ this factor equals $\mathrm{tr}\underline{E} > 1$, and at other times this enhancement is further acted on by the affine flow operator $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_t^T$. Thus on long scales we recover equilibriumlike statistics, i.e., a generalized random walk each step of which obeys modified statistics with nonvanishing correlations between different Cartesian components (the step correlation matrix being $\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t$). The end-to-end distance of this random walk is always greater than that in equilibrium regardless of the particular form of the flow.

As remarked in the Introduction, Lindner and Oberthur [42,43] have measured the equal time coherent scattering function $S_{\rm coh}$ for dilute polymer solutions in *constant* shear flows of strengths extending into the nonlinear region, $\Omega\tau_0 \gtrsim 1$. Anisotropy of the polymer configuration was observed, chains being stretched in a certain direction (whose orientation is shear dependent) but not in other directions. Since [42,43] a polymer "tumbles" of order one time per relaxation time in the presence of constant shear, we may, very crudely speaking, compare the constant shear flows used in these experiments with the situations studied here by substituting $\omega \approx 1/\tau_0$, $\lambda \approx \Omega\tau_0$. These authors deduced, using their data in conjunction with the light-scattering data of Cottrell, Merill, and Smith [41], that the polymer coil volume, calculated on the basis of the end-to-end vector, was reduced by the flow. This is reminiscent, of course, of the situation in the present work: in proving that $\det\underline{E} \geq 1$ [Eq. (27)] we have proved that the coil volume is reduced by our oscillatory flow. The observed chain stretching and coil volume reduction match (to within constant prefactors) our results if one uses the appropriate value for λ. At large wave vectors, corresponding to small scales within the polymer, it was observed [42,43] that the perturbation away from equilibrium was much reduced compared with the large scales. Indeed, in the following section such small scales are considered and we will see that scales within the so-called "Ω blob" are very close to equilibrium in our time-dependent flows.

V. SMALL-SCALE BEHAVIOR

Up to this point we have concentrated on the long-wavelength behavior in time and space where the behavior is "affine." These scales are more easily accessed experimentally and possess, moreover, more universal features than the small scales (see below). In this section we will investigate both equal time quantities (the separation between two nearby chain units) and the displacement of a single chain unit for small times. By "nearby" and "small" here we mean scales within the "ω blob" size and less than the blob relaxation time $1/\omega$. Recall [see Eq. (58)] that the definition of this "blob" was that its relaxation time just matches the flow period. Let us define in a similar manner the "Ω blob" to be a portion of polymer containing s_Ω units with relaxation time equal to $1/\Omega$:

$$\tau_{s_\Omega} = \frac{1}{\Omega}, \quad s_\Omega = (\Omega\zeta)^{1/2} , \quad (79)$$

where $\tau_s \equiv \zeta s^2/\pi^2$ denotes the relaxation time of a portion of polymer containing s units. Now τ_s itself defines a "$1/\tau_s$ blob." Then if we seek the behavior on polymer scales s or time scales $t-t_0$, the situation is fully characterized by the relative positions of the Ω, ω, τ_s^{-1}, and $(t-t_0)^{-1}$ blobs as illustrated in Fig. 5. We are assuming the τ_0^{-1} blob is far outside any of these, i.e., the Rouse time is effectively infinite.

Now the only requirement for validity of our analysis of large-scale behavior was that the scales involved be "outside" the ω blob; the size of Ω is not a criterion in this respect. Though the results depended on Ω, since they turned out to be governed by $\lambda \equiv \Omega/\omega$, their validity does not. For small scales the story is very different. Depending on whether the Ω blob lies within or outside the ω blob we will see that the behavior is different, i.e., the value of λ is the determinant of the nature of the behavior. We now consider the small-scale behavior for the three cases illustrated schematically in Fig. 5, namely, $\lambda \approx 1$, $\lambda \ll 1$, and $\lambda \gg 1$.

A. λ of order unity

For short times and scales this situation is depicted in Fig. 5(b), where the Ω blob and ω blob are shown coincident (in an order-of-magnitude sense). Consider first the spatial separation at time t between two points on the polymer which are $s(\ll s_\Omega, s_\omega)$ chain units apart. The relative position vector is conveniently expressed in terms of the real-space Green's function (i.e., s):

$$\langle \mathbf{R}(s,t)\mathbf{R}(s,t)\rangle = \frac{2}{\zeta}\int_{-\infty}^{t} dt' e^{\underline{A}\int_{t'}^{t}\Omega(t'')} e^{\underline{A}^T\int_{t'}^{t}\Omega(t'')}\left[\frac{1-\exp[-\tau_s/8(t-t')]}{[2\pi(t-t')\zeta^{-1}]^{1/2}}\right]$$

$$= \frac{2}{\sqrt{\omega\zeta}}\int_0^\infty du\, e^{\underline{A}\lambda\int_{\omega t-u}^{\omega t}} e^{\underline{A}^T\lambda\int_{\omega t-u}^{\omega t}} g\left[\frac{1-\exp(-\omega\tau_s/8u)}{\sqrt{2\pi u}}\right], \quad \tau_s \equiv s^2\zeta\,, \tag{80}$$

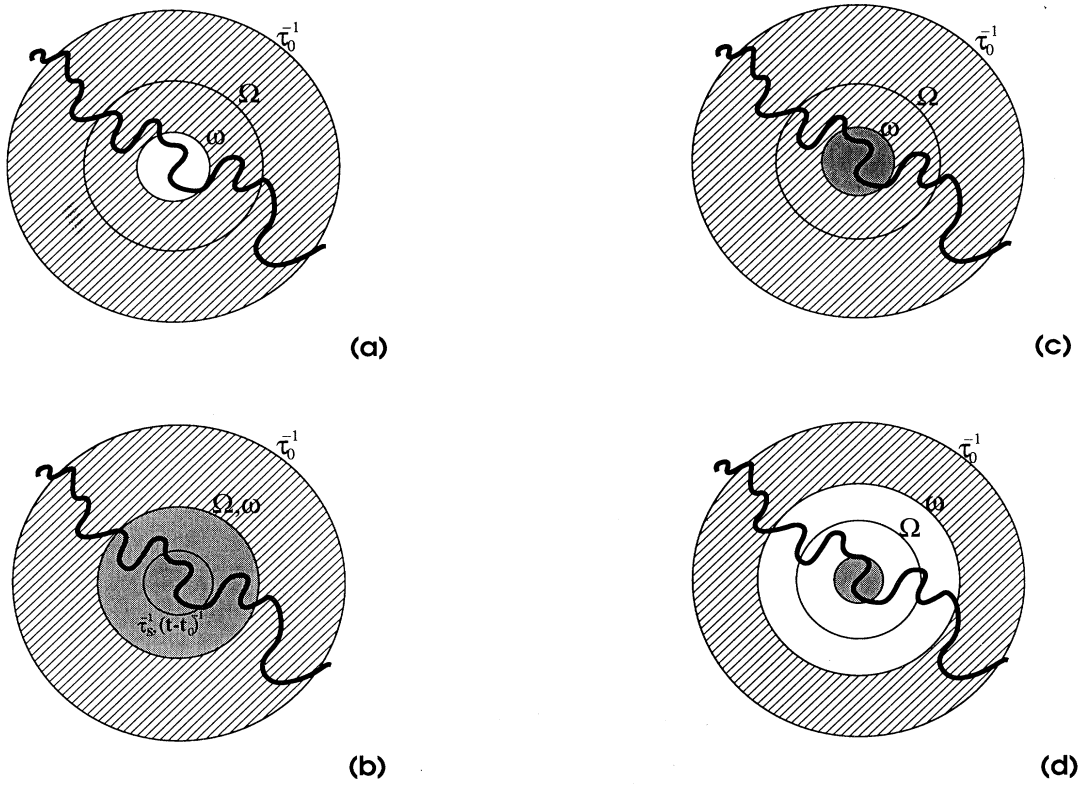

FIG. 5. (a) Each blob defines a scale within the polymer whose relaxation rate equals its frequency label. Polymer modes are excited when the Ω blob and ω blob lie within the τ_0^{-1} blob. The shaded region outside the ω blob represents all those scales which respond affinely to the flow; their relaxation times are too great to respond to changes in the flow field (which occur on a time scale $\sim 1/\omega$). The band outside the ω blob ($s > s_\omega$) is always affine regardless of the value of $\lambda \equiv \Omega/\omega$, i.e., regardless of the relative positions of the Ω blob and ω blob. (b) The physical behavior on a certain polymer scale involving $\sim s$ chain units, or on a certain time scale $t - t_0$, is characterized by the relative positions of the ω blob, Ω blob, τ_s^{-1} blob, and $(t-t_0)^{-1}$ blob. Illustrated here is the case when $\lambda = O(1)$ (so the Ω blob and ω blob coincide in an order-of-magnitude sense) and the scales of interest lie in the inner gray region, i.e., $s < s_\omega, s_\Omega$. For $\lambda = O(1)$ all scales in this gray band are quasistatic, having static and dynamic behavior close to that in equilibrium. The shaded band is affine. (c) The linear regime, $\lambda \ll 1$. The shaded and gray bands are affine and quasistatic, respectively. The position of the Ω blob relative to the τ_0^{-1} blob is in fact irrelevant. (d) The strongly nonlinear regime, $\lambda \gg 1$. Equilibrium behavior applies only for scales exponentially smaller than the Ω blob (the gray region). The band between the gray band and the shaded affine band is a complex crossover region.

where we have used $\Omega(t)=\Omega g(\omega t)$. The above expression can be obtained from the Rouse equation, Eq. (46), by substituting $\mathbf{r}(s,t)\equiv\underline{\Gamma}_t\mathbf{x}(s,t)$ and solving the resultant equation for $\mathbf{x}$ [which is another Rouse equation with a modified random force $f(t)\rightarrow\underline{\Gamma}_t^{-1}f(t)$ and with no flow term] in terms of the s-space Rouse Green's function G. This gives an expression for $\langle\mathbf{R}(s,t)\mathbf{R}(s,t)\rangle$ involving the expression in square brackets above operating on $\underline{\Gamma}_{t'}^{-1}\underline{\Gamma}_{t'}^{-1T}$ on which $\underline{\Gamma}_t\cdots\underline{\Gamma}_t^T$ acts from the outside since $\mathbf{r}=\underline{\Gamma}_t\mathbf{x}$. Bringing these outer operators inside the integrand one obtains the above expression. In the cases of pure extensional and shear flows, this calculation was explicitly performed in Ref. [3]; the reader is referred there for details.

Now consider the case $s_\Omega\leq s_\omega$ (the aim being to leave our results adaptable to the case of $\lambda\gg1$ to be treated in the next section). Then the smallest scales are always defined by $s\ll s_\Omega$; for these scales it is in fact easier to deal with the modes, so we rewrite Eq. (80)

$$\langle\mathbf{R}(s,t)\mathbf{R}(s,t)\rangle=\frac{4s}{\pi}\mathrm{Re}\int_0^\infty dq(1-e^{iq})\int_0^\infty dX\exp\left[\underline{A}\lambda\int_{\omega t-\omega\tau_s X}^{\omega t}g\right]\exp\left[\underline{A}^T\lambda\int_{\omega t-\omega\tau_s X}^{\omega t}g\right]e^{-2q^2X}\ . \tag{81}$$

Let us split up the q integral as

$$\int_0^\infty dq=\int_0^{(\omega\tau_s)^{1/2}}dq+\int_{(\omega\tau_s)^{1/2}}^{(\Omega\tau_s)^{1/2}}dq+\int_{(\Omega\tau_s)^{1/2}}^\infty dq\equiv\int_1+\int_2+\int_3\ .$$

The dominant part is $\int_3$, in which $\int dX$ has width $\Delta X\sim1/q^2\ll1$ ($s\ll s_\Omega$) so the matrix exponentials can be expanded. The leading term from $\int dX$ is $\int_0^\infty dX\exp\{-2q^2X\}=1/2q^2$ which gives s (the equilibrium result) after integrating over q plus relative errors of order $(\omega\tau_s)^{1/2}$ and $\lambda(\Omega\tau_s)^{1/2}$. Then both $\int_1$ and $\int_2$ give relative corrections of order $\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T(\omega\tau_s)^{1/2}$ (in $\int_1$ the affine result applies and one preaverages the oscillatory term). Thus

$$\langle\mathbf{R}(s,t)\mathbf{R}(s,t)\rangle=s\underline{I}[1+O(\lambda(\Omega\tau_s)^{1/2},\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T(\omega\tau_s)^{1/2})],\quad\omega\tau_s,\Omega\tau_s\ll1\ . \tag{82}$$

This result tells us that on small scales equilibrium statistics are recovered to within small corrections. On such scales the dimensionless flow strength $\Omega\tau_s$ is weak; the strength is the appropriate parameter for "quasistatic" scales, namely, polymer scales which have sufficient time to relax before the flow has substantially changed. This should be compared with the affine scales which deform with the fluid; there λ is the appropriate measure of the effect of the flow. When $\lambda=O(1)$, this means the scales on which equilibrium statistics are recovered are identified with the Ω blob [see Fig. 5(b)].

Now we consider the displacement of a chain unit for times much less than the flow period. Now as for the affine scales we must carefully separate off the center of gravity and "elastic band" contributions to the motion; these are effectively infinite (i.e., of the order of the polymer size and the size of the entire system) even at small times. Consider the basic expression for the displacement correlation function, Eq. (53):

$$\langle\mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle=\langle[\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle+\left[\frac{2}{N}\right]\sum_{p=1}^\infty\cos^2\left[\frac{p\pi s}{N}\right]\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle\ . \tag{83}$$

Writing the result for the mode correlation function, Eq. (56), in the form

$$\begin{aligned}\langle\mathbf{r}_p(t)\mathbf{r}_p(t_0)\rangle&=\underline{\Gamma}_t\underline{Y}_t^p\underline{\Gamma}_{t_0}^Te^{-(t-t_0)/\tau_p}\ ,\\ \underline{Y}_t^p&\equiv\frac{2}{\zeta}\int_{-\infty}^t dt'e^{-2(t-t')/\tau_p}\underline{\Gamma}_{t'}^{-1}(\underline{\Gamma}_{t'}^{-1})^T\\ &=\frac{2\tau_p}{\zeta}\int_0^\infty du\,e^{-2u}\underline{\Gamma}_{t-u\tau_p}^{-1}(\underline{\Gamma}_{t-u\tau_p}^{-1})^T\ ,\end{aligned} \tag{84}$$

we can express the mode average appearing in Eq. (83) as

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle=\underline{\Gamma}_t\underline{Y}_t^p\underline{\Gamma}_t^T+\underline{\Gamma}_{t_0}\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T-[\underline{\Gamma}_t\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T+\underline{\Gamma}_{t_0}\underline{Y}_{t_0}^p\underline{\Gamma}_t^T]e^{-(t-t_0)/\tau_p}\ . \tag{85}$$

Now the deterministic part of the evolution (i.e., the evolution without random force) is given in Eq. (59). Substituting for the mode correlations from Eq. (84) we have

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\mathrm{det}}=(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-1)\underline{\Gamma}_{t_0}\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T(\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}-1)\ . \tag{86}$$

Thus the random part of the evolution is given by

$$\begin{aligned}\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\mathrm{ran}}&\equiv\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle-\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\mathrm{det}}\\ &=\underline{\Gamma}_t(\underline{Y}_t^p-\underline{Y}_{t_0}^p)\underline{\Gamma}_t^T+2[\underline{\Gamma}_t\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T]^S(1-e^{-(t-t_0)/\tau_p})\ .\end{aligned} \tag{87}$$

As we will see in a moment, this random part is a "good" local quantity, in that it does not depend on the size of the polymer which diverges as $N\to\infty$; all such divergent N dependence occurs in the deterministic and center-of-gravity terms.

In Sec. III we considered affine modes for which we can preaverage the time-dependent flow operators in the integral defining $\underline{Y}_t^p$, leading to $\underline{Y}_t^p \approx \underline{E}\tau_p/\zeta = \underline{E}\langle \mathbf{r}_p(t)\mathbf{r}_p(t)\rangle^{\rm eq}$ independent of time. Then Eq. (87) reduces to

$$\langle\cdots\rangle^{\rm ran}\approx 2[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S\langle \mathbf{r}_p(t)\mathbf{r}_p(t)\rangle^{\rm eq} \times\{1-\exp[-(t-t_0)/\tau_p]\}$$

which is just the equilibrium result operated on by $[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S$. Summing over modes then led to the equilibrium result times this same operator, Eq. (65).

For "quasistatic" modes, since $\omega\tau_p \ll 1$ we can expand the $\underline{\Gamma}$ factors in the u integrand defining $\underline{Y}_t^p$ in Eq. (84) for small $u\tau_p$; this is so because the integrand has width $\Delta u\sim 1$ so $u\tau_p\sim\tau_p$ which is much less than the time $1/\omega$ in which $\underline{\Gamma}_{t-u\tau_p}^{-1}$ changes. Thus we expand $\underline{\Gamma}_{t-u\tau_p}^{-1} = \underline{\Gamma}_t^{-1} - u\tau_p\underline{\Gamma}_t^{-1} + \cdots = \underline{\Gamma}_t^{-1}(1 + u\underline{A}\,\Omega(t)\tau_p + \cdots)$. For the correction term to be small, note that we need $\Omega\tau_p \ll 1$. This point will be discussed further in the next section. Expanding thus for $\underline{\Gamma}_{t-u\tau_p}^{-1}$ in Eq. (84) one finds to leading order

$$\underline{Y}_t^p = \underline{\Gamma}_t^{-1}\frac{\tau_p}{\zeta}\{1+\underline{A}\,{}^S\Omega(t)\tau_p+\cdots\}(\underline{\Gamma}_t^{-1})^T, \quad \omega\tau_p,\Omega\tau_p\ll 1 . \tag{88}$$

Thus

$$[\underline{\Gamma}_t\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T]^S \approx \left[\underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\frac{\tau_p}{\zeta}\{1+\underline{A}\,{}^S\Omega(t_0)\tau_p+\cdots\}\right]^S, \quad \omega\tau_p,\Omega\tau_p\ll 1 . \tag{89}$$

Using Eq. (88) the first term appearing on the right-hand side of Eq. (87) approximates

$$\underline{\Gamma}_t(\underline{Y}_t^p-\underline{Y}_{t_0}^p)\underline{\Gamma}_t^T \approx \frac{\tau_p}{\zeta}[1+\underline{A}\,{}^S\Omega(t)\tau_p] - \underline{\Gamma}_t\underline{\Gamma}_{t_0}^{-1}\frac{\tau_p}{\zeta}[1+\underline{A}\,{}^S\Omega(t_0)\tau_p](\underline{\Gamma}_{t_0}^{-1})^T\underline{\Gamma}_t^T, \quad \omega\tau_p,\Omega\tau_p\ll 1 . \tag{90}$$

So far we have not exploited the smallness of $t-t_0$. When $\Omega(t-t_0),\omega(t-t_0)\ll 1$ we can further expand the deterministic propagator according to Eq. (43). Using this in Eqs. (89) and (90) yields

$$[\underline{\Gamma}_t\underline{Y}_{t_0}^p\underline{\Gamma}_{t_0}^T]^S \approx \frac{\tau_p}{\zeta}[1+\underline{A}\,{}^S\Omega(t_0)(t-t_0)+\underline{A}\,{}^S\Omega(t_0)\tau_p],$$

$$\underline{\Gamma}_t(\underline{Y}_t^p-\underline{Y}_{t_0}^p)\underline{\Gamma}_t^T \approx \frac{\tau_p\underline{A}^S}{\zeta}[-2\Omega(t_0)(t-t_0)], \quad \Omega(t-t_0),\omega(t-t_0)\ll 1 . \tag{91}$$

We have used the fact that $\Omega(t)$ and $\Omega(t_0)$ are the same as one another to within a higher-order term:

$$\tau_p[\Omega(t)-\Omega(t_0)] = \Omega\tau_p[g(\omega t_0)+\omega(t-t_0)g'(\omega t_0)-g(\omega t_0)] = \Omega\tau_p\omega(t-t_0)g'(\omega t_0) .$$

The above results enable us to express the random part of the mode evolution, Eq. (87), as

$$\langle[\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\rm ran} \approx 2\frac{\tau_p}{\zeta}[1-e^{-(t-t_0)/\tau_p}]+2\underline{A}\,{}^S\Omega(t_0)\frac{\tau_p^2}{\zeta}[1-e^{-(t-t_0)/\tau_p}] -2\underline{A}\,{}^S\Omega(t_0)(t-t_0)\frac{\tau_p}{\zeta}e^{-(t-t_0)/\tau_p}, \quad \omega\tau_p,\Omega\tau_p,\Omega(t-t_0),\omega(t-t_0)\ll 1 . \tag{92}$$

The first term above is just the result one obtains when there is no flow. The other two terms are higher order. In the following we will assume $\Omega\tau_p\geq\omega\tau_p$ (i.e., $\lambda\geq 1$). If we assume we can use the above form for *all* modes, including affine modes, then we deduce that the random part of the correlation function, after mode summation, just gives the equilibrium result $C[(t-t_0)/\zeta]^{1/2}$ plus corrections. Consider first the correction term arising from using the equilibrium leading term belonging to the above quasistatic form in the band $0<q<q_\omega$ where it does not actually apply (we convert to $q\equiv p\pi/N$ for convenience). This is of order

$$\int_0^{q_\omega}\{\tau_q/\zeta\}[1-\exp\{-(t-t_0)/\tau_q\}] \approx[(t-t_0)/\zeta]q_\omega=[(t-t_0)/\zeta](\omega\zeta)^{1/2},$$

where we used $\tau_q=\zeta/q^2$ and we expanded the exponential since $\tau_q\gg(t-t_0)$ in the domain of integration for small $\omega(t-t_0)$. Therefore the correction relative to the leading-order term $[(t-t_0)/\zeta]^{1/2}$ is of order $[\omega(t-t_0)]^{1/2}\ll 1$. Another correction arises from neglecting the affine modes' contribution and is of order

$$[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S\int_0^{q_\omega}\frac{\tau_q}{\zeta}[1-\exp\{-(t-t_0)/\tau_q\}] \approx\left[\frac{(t-t_0)}{\zeta}\right]^{1/2}[\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T]^S[\omega(t-t_0)]^{1/2} . \tag{93}$$

Note that the elements of the $\underline{\Gamma}_t$ factors are all of order unity in the case $\lambda\approx 1$. One sees from Eq. (93) that this correction is then of the same order as that we considered

first, i.e., of order $[\omega(t-t_0)]^{1/2} \ll 1$.

Now consider the correction due to the $\Omega(t-t_0)\tau_p/\zeta$ term in Eq. (92). The latter of these two contributes

$$\sim \Omega(t-t_0)\int_{q_\Omega}^{\infty} q^{-2}\exp\{-q^2(t-t_0)/\zeta\} \approx \Omega(t-t_0)\int_{q_\Omega}^{[\zeta/(t-t_0)]^{1/2}} q^{-2} \approx \Omega(t-t_0)/q_\Omega$$

(the exponential selects the band $q_\Omega < q < [\zeta/(t-t_0)]^{1/2}$) which gives a correction relative to the no-flow result of order $[\Omega(t-t_0)]^{1/2}$ which is of order $[\Omega(t-t_0)]^{1/2}$.

Lastly consider the $\Omega\tau_p^2/\zeta$ term in Eq. (92) which after mode summation gives

$$\Omega\zeta\int_{q_\Omega}^{\infty}(1/q^4)\{1-\exp[-q^2(t-t_0)/\zeta]\} = \Omega\zeta[(t-t_0)/\zeta]^{3/2}\int_{[\Omega(t-t_0)]^{1/2}}^{\infty}[1-\exp(-u^2)]/u^4 \ .$$

This last integral is dominated by the lower limit which is much less than unity, giving $\sim 1/[\Omega(t-t_0)]^{1/2}$. The net contribution is thus $[(t-t_0)/\zeta]^{1/2}\Omega(t-t_0)/[\Omega(t-t_0)]^{1/2}$ and so the relative correction is of order $\lambda[\Omega(t-t_0)]^{1/2}$.

Having determined the effect of the correction terms, Eq. (92) in Eq. (83) gives

$$\begin{aligned}\langle \mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle &= \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle \\ &+ \left[\frac{2}{N}\right]\sum_{p=1}^{\infty}\cos^2\left[\frac{p\pi s}{N}\right]\langle [\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\det} \\ &+ \left\{C\left[\frac{t-t_0}{\zeta}\right]^{1/2}\right\}\{1+O(\lambda[\omega(t-t_0)]^{1/2})\}, \quad \omega(t-t_0)\ll 1, \quad \lambda = O(1) \ , \end{aligned} \tag{94}$$

where the deterministic part of the mode evolution is given in Eq. (86). Using the small-time form in Eq. (43) one has

$$\begin{aligned}\langle [\mathbf{r}_p(t)-\mathbf{r}_p(t_0)][\mathbf{r}_p(t)-\mathbf{r}_p(t_0)]\rangle^{\det} &= [\underline{A}\,\Omega(t_0)(t-t_0)+O(\Omega\omega(t-t_0)^2,[\Omega(t-t_0)]^2)]\underline{\Gamma}_{t_0}\underline{Y}^p_{t_0}\underline{\Gamma}^T_{t_0} \\ &\times[\underline{A}^{\,T}\Omega(t_0)(t-t_0)+O(\Omega\omega(t-t_0)^2,[\Omega(t-t_0)]^2)] \\ &= [\Omega(t-t_0)]^2\underline{A}\langle \mathbf{r}_p(t_0)\mathbf{r}_p(t_0)\rangle\underline{A}^{\,T} \\ &\times[1+O(\Omega(t-t_0),\omega(t-t_0))], \quad \omega(t-t_0),\Omega(t-t_0)\ll 1 \ , \end{aligned} \tag{95}$$

where we used Eq. (84) to obtain the equal time mode correlation. Now if we used the *affine* mode form, Eq. (57), which is $\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T$ times the equilibrium value, then from Eqs. (62) and (63) the mode summation would produce $\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T$ times the correlation of the position of the sth chain unit relative to the center of gravity for a chain in equilibrium, Eq. (63). This of course is precisely what we obtained for long times. For these small times we must check that this factor is still dominated by the affine modes. To estimate the quasistatic modes' contribution for these small times, the factor $\underline{\Gamma}_{t_0}\underline{Y}^p_{t_0}\underline{\Gamma}^T_{t_0}$ can be expanded as in Eq. (89) which on summing over modes gives a contribution bounded by (set the cosine to unity) $\int_{q_\Omega}^{\infty}(\tau_q/\zeta)\sim(\Omega\zeta)^{1/2}$ from the τ_p leading term in the expansion. In fact the correction term of order $\Omega\tau_p^2/\zeta$ contributes by an amount of the same order as does the correction term from the summation of the affine mode form in the quasistatic band ($\sim\underline{E}\int_{q_\Omega}^{\infty}\tau_q/\zeta$). But these corrections should be compared to the affine result which is of order $\underline{N}$; the relative contribution is $O(\Omega\tau_0)^{1/2}\ll 1$. The final result therefore reads

$$\begin{aligned}\langle \mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle &\approx \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle \\ &+[\Omega(t-t_0)]^2\underline{A}\,\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_t^T\underline{A}^{\,T}\left\{N\left[\left[\frac{s}{N}\right]^2-\left[\frac{s}{N}\right]+\frac{1}{3}\right]\right\}+\left\{C\left[\frac{t-t_0}{\zeta}\right]^{1/2}\right\}, \\ &\omega\tau_0,\Omega(t-t_0),\omega(t-t_0)\ll 1, \quad \lambda=O(1) \ , \end{aligned} \tag{96}$$

with relative corrections of the order of $\omega\tau_0$, $\Omega(t-t_0)$, and $\omega(t-t_0)$. We see that the fluctuation term is as in equilibrium, characterized by the unenhanced diffusivity. Thus in this sense for small times the chain unit displacement is as without flow. However, there is an important flow effect which survives even at these small times; it is very important that one does not discard the $[\Omega(t-t_0)]^2$ term as being of higher order, since it multiplies an "infinite" term of order $\underline{N}$. A similar issue arose when we considered the small-time center-of-gravity dynamics Eq. (45) where a second-order quantity is multiplied by an "infinite" initial position. The "infinite" term in Eq. (96)

is the "elastic band" term; the entire polymer is stretched and undergoes periodic elongation and contraction from the flow which moves the sth chain unit by amounts of the order of the chain size.

B. The linear regime: $\lambda \ll 1$

Here the Ω blob lies well outside the ω blob as shown in Fig. 5(c); clearly linearity applies on all scales since small λ implies small affine deformation of the polymer on long scales which in turn means the small scales cannot be strongly deformed relative to equilibrium. Therefore all quantities will be close to equilibrium and we seek the form of leading-order corrections. In addition to linear small-scale forms, in this section we will include some first-order truncations of affine results in order to present a complete picture of the linear regime.

Consider first the equal time relative position vector of two points on the chain separated by s units from each other. Now from the expression in Eq. (80) it is clear that for small λ we can expand the matrix exponentials:

$$\langle \mathbf{R}(s,t)\mathbf{R}(s,t)\rangle = s\underline{I} + \frac{2\lambda(\underline{A}+\underline{A}^T)}{\sqrt{\omega\zeta}} \int_0^\infty du \int_{\omega t-u}^{\omega t} g \left[\frac{1-\exp(-\omega\tau_s/8u)}{\sqrt{2\pi u}} \right] + O(\lambda)^2 , \tag{97}$$

where the first term is just the equilibrium random walk result. Notice first that the square bracket term [ ] above becomes small when $u \gg \omega\tau_s$. Now if $\omega\tau_s \gg 1$ [i.e., s belongs to affine scales much greater than the size of the ω blob, see Fig. 5(c)] then the [ ] factor decays very slowly relative to the integral of the g factor since the latter has period of order unity [see Eq. (3)]. But the integral of the periodic g is also periodic since g has zero mean; therefore we may to a good approximation replace this factor by its average over a period. Writing $\int_{\omega t-u}^{\omega t} g = \int_0^{\omega t} g - \int_0^{\omega t-u} g$ one obtains

$$\begin{aligned}\langle \mathbf{R}(s,t)\mathbf{R}(s,t)\rangle &\approx s\underline{I}\left[1+\lambda(A+A^T)\left\{\int_0^{\omega t} g - \left\langle \int_0^u g(u)\right\rangle_u\right\}\right] \\ &= s\underline{I}\left[1+\lambda(A+A^T)\left\{\int_0^{\omega t} g\right\}\right], \quad \omega\tau_s \gg 1 .\end{aligned} \tag{98}$$

This result is characteristic of affine scales in that it depends on λ, the degree of deformation of the chain which on large scales moves with the fluid without relative slip. The above result is simply the result for general λ in the affine region, Eq. (78), expanded to leading order (i.e., the expansion of the enhancement tensor). This reflects the irrelevance of the value of Ω to the actual form of the result; no matter "where" the Ω blob is, behavior of all scales outside the ω blob is of the same form.

Now for small scales s which lie well inside the ω blob, $\omega\tau_s \ll 1$ [see Fig. 5(c)], $\langle RR \rangle$ will be the same as for the finite λ case, Eq. (82), since that result relied only on the τ_s^{-1} blob being inside the ω blob and the Ω blob; but the latter is automatically implied by the former in the linear regime. As remarked following Eq. (82), this is a "quasistatic" result. Small scales have enough time to adjust to the changing flow field; if the flow strength is less than the natural restoring force of the blob of s monomers (which is proportional to $1/\tau_s$) then such a scale experiences the flow as if it were a time-independent one with the instantaneous flow value. In an unchanging flow it is its *strength* which matters; $\Omega\tau_s$ is the dimensionless measure of this. Note that for both the above quasistatic and affine results there is no linear effect on the mean-square separation which is the trace of $\langle \mathbf{R}(s,t)\mathbf{R}(s,t)\rangle$; changes in the size of the polymer are second order in λ for affine scales and second order in $\Omega\tau_s$ for quasistatic scales.

Now in Sec. III we calculated the mean-square displacement of a chain unit for large times relative to the flow period, Eq. (65). Before considering the small-time behavior, it is helpful to specialize the result of Eq. (65) to the linear case. Expanding that result for small λ (the relevant parameter for "affine" scales) one immediately finds

$$\begin{aligned}\langle \mathbf{d}(s,t_0,t)\mathbf{d}(s,t_0,t)\rangle &= \langle [\mathbf{R}_G(t)-\mathbf{R}_G(t_0)][\mathbf{R}_G(t)-\mathbf{R}_G(t_0)]\rangle \\ &+ \lambda^2 \left[\int_{t_0}^t g\right]^2 \underline{A}\,\underline{A}^T \left\{ N\left[\left[\frac{s}{N}\right]^2 - \left[\frac{s}{N}\right] + \frac{1}{3}\right]\right\} \\ &+ \left[1+\lambda\frac{(A+A^T)}{2}\left\{\int_0^{\omega t} g + \int_0^{\omega t_0} g\right\}\right] C\left[\frac{t-t_0}{\zeta}\right]^{1/2} + O(\lambda^2), \quad \omega^{-1} \ll t-t_0 \ll \tau_0 .\end{aligned} \tag{99}$$

Notice that the "elastic band" term in Eq. (99) describing the periodic deformation of the stretched polymer is of second order in λ but multiples a term of order $\underline{N}$ and so must not be discarded. In fact there are other corrections to the above expression of order $1/[\omega(t-t_0)]^{1/2}$ (see Appendix B) due to the error in the affine approximation itself.

Finally, for small times in the linear regime we can

simply take the finite λ result Eq. (96) and expand for small λ. The result is unchanged, except for the replacement in the "elastic band" term $\underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_t^T \rightarrow 1$.

C. $\lambda \gg 1$

This is a somewhat unphysical regime [see Fig. 5(d)] in which the chain is highly extended when the absence of finite extensibility effects in our model is crucial. However, it is of theoretical interest and at least should be amenable to computer experimentation.

Large λ in no ways upsets the affine calculations of course. For the "smallest" scales, one recovers all the results for finite λ (i.e., essentially equilibrium fluctuations plus the "elastic band" term), but the definition of "small" must be revised. Consider the equal time separation for small scales, Eq. (82); the criterion is that the τ_s^{-1} blob lie within the ω blob and the Ω blob for $\lambda = O(1)$. For large λ, however, the correction terms are evidently small only when the elements of $(\Omega\tau_s)^{1/2}\underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_t^T$ are much less than unity. Roughly then we require

$$(\Omega\tau_s)^{1/2} \ll e^{-\text{const}\times\lambda}, \quad s \ll s_\Omega e^{-\text{const}\times 2\lambda} \tag{100}$$

for equilibrium statics to prevail, where the value of the positive constant depends on the largest positive real part of the eigenvalues of $\underline{A}$ (for the special case of shear the λ dependence is polynomial). For large λ this defines a blob which is exponentially smaller than the Ω blob. Note that the complex band of scales between this innermost blob and the ω blob is neither of affine nor equilibrium character; rather it is a crossover regime [see Fig. 5(d)].

A similar story is true for dynamics. When $\lambda \gg 1$ we must consider all the correction terms evaluated in the preceding section, but now there is an extra contribution deriving from modes in the band between the Ω blob and ω blob [see Fig. 5(d)], namely, $\int_{q_\omega}^{q_\Omega} dq \langle [\mathbf{r}_p(t) - \mathbf{r}_p(t_0)][\mathbf{r}_p(t) - \mathbf{r}_p(t_0)] \rangle^{\text{ran}}$. Now in Eq. (87) the magnitudes of the elements of $\underline{Y}_t^p$ are monotonic, decreasing with increasing p [see Eq. (84)]. Thus for $\underline{Y}_t^p$ in Eq. (84) we can use the affine result at $p = p_\omega$ to bound this correction. Then the second term on the right-hand side of Eq. (87) gives a leading term of order

$$[\underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_{t_0}^T]^S \int_{q_\omega}^{q_\Omega} \frac{1}{q_\omega^2}(1 - e^{-q^2(t-t_0)/\zeta}) \approx \left[\frac{t-t_0}{\zeta}\right]^{1/2} [\underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_{t_0}^T]^S \lambda [\Omega(t-t_0)]^{1/2}, \tag{101}$$

where the exponential was expanded assuming $\Omega(t-t_0) \ll 1$. Similarly, expanding the first term on the right-hand side of Eq. (87) for $\Omega(t-t_0) \ll 1$ at $p = p_\omega$, one obtains a correction term of the same order.

Looking back at the $\lambda = O(1)$ section, when $\lambda \gg 1$ the dominant error term among those calculated arises in Eq. (93): this is of order $[(t-t_0)/\zeta]^{1/2}[\underline{\Gamma}_t \underline{E}\, \underline{\Gamma}_{t_0}^T]^S [\omega(t-t_0)]^{1/2}$. In summary, for $\lambda \gg 1$ equilibrium forms for chain unit displacement are recovered when times are so small that

$$[\Omega(t-t_0)]^{1/2} \ll e^{-\text{const}\times\lambda}, \quad t - t_0 \ll \frac{1}{\Omega} e^{-\text{const}\times 2\lambda}, \tag{102}$$

where all corrections were compared to the leading term $[(t-t_0)/\zeta]^{1/2}$. These are time scales which for large λ are exponentially smaller than $1/\Omega$ [see Fig. 5(d)].

The interesting physical feature peculiar to the large λ regime is the feeding down to small scales from the large affine scales which are strongly stretched. The scale at which equilibrium statistics are recovered, i.e., at which the flow is a weak perturbation, is much less than the inverse of the first mode for which this is the case, namely, q_Ω (note one requires both $q < q_\omega$ and $q < q_\Omega$ for "quasistatic" to be a good label since for modes in between these two scales "runaway" occurs). All modes $q < q_\Omega$ are quasistatic, being weakly perturbed by the flow which changes slowly relative to their relaxation time scales; however, when $\lambda \gg 1$ this is not true of all of the scales, $1/q$, which one usually associates with that band of modes. The usual real-space–reciprocal-space relationship is upset in this strongly nonlinear regime. Loosely, one can compare this to a situation in which a polymer chain's ends are held apart a distance λ times the equilibrium rms end-to-end distance. For large λ the statistics are linear down to a very small scale where random walk statistics are recovered.

VI. CONCLUSIONS

In the present work the behavior of dilute solutions under periodic flows has been considered. Our interest has been in nonlinear effects resulting from interactions between the macroscopic flow and the microscopic fluctuations of the solute molecules.

Generally, a single solute particle has internal degrees of freedom with some longest relaxation time τ_0 (for example, in the case of dilute polymers τ_0 is the longest polymer relaxation time). In Sec. II we considered flows whose characteristic time scales $1/\omega$ and $1/\Omega$ were both far greater than τ_0; the physical situation is symbolically represented in Figs. 6(a) and 6(b). Then there is no interaction between flow and internal particle time scales so the particle is justifiably treated as pointlike, i.e., without internal structure. This is the simple center-of-gravity Langevin equation plus flow which was analyzed in Sec. II and for these reasons is a good description of any dilute system, polymeric or not. Explicitly, the internal degrees of freedom are only very weakly excited since the "τ_0^{-1} blob" is far inside the ω blob; this means the flow is effectively constant for the internal degrees of freedom whose response is quasistatic and is determined by the dimensionless flow strength $\Omega\tau_0$ which is much less than unity since the Ω blob is far outside the τ_0^{-1} blob. The relative "position" of the ω blob and the Ω blob (i.e., the value of λ) does not affect this, i.e., for either of the situations in Figs. 6(a) and 6(b) the deformation of the particle is very small, i.e., internal modes are very weakly excited.

It was found that in flows with vanishing time-averaged velocity gradient the fluctuations in particle positions grow for large times as in equilibrium but with the

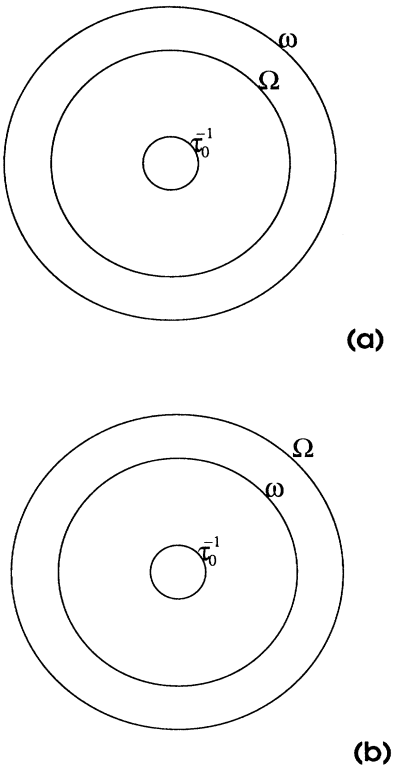

FIG. 6. (a) The analysis of Sec. II is valid when the flow blobs lie well outside the τ_0^{-1} blob; this guarantees that internal modes are unexcited regardless of the value of λ. Here the case $\lambda \gg 1$ is illustrated. Scales outside the ω blob are affine just as for the polymer situations of Fig. 5. A new regime prevails when flow blobs "enter" the longest relaxation τ_0^{-1} blob. This is the situation dealt with in Fig. 5. (b) $\lambda \ll 1$.

diffusivity $\underline{D}$ replaced by $\tilde{\underline{D}}$ together with a periodic flow deformation via the operator $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_t^T$. These two effects are very different; the latter is an instantaneous pure flow effect, the former an accumulated long-time flow-fluctuation interactive effect. This means that the growth in the size of a cloud of particles is anisotropic and enhanced (relative to no flow) by such periodic flows as described by the enhancement tensor $\underline{E}$ of Eq. (13). Roughly, one can say that on time scales less than $1/\Omega$ diffusion wins over the flow; on longer time scales the resultant diffusive "cloud" gets stretched by the flow. This stretching continues for a time $\sim 1/\omega$; the net stretching thus produces a displacement (one step) which depends on $\Omega\omega^{-1}=\lambda$. After $1/\omega$ the flow changes and the process repeats itself in an independent way. The end result is a random walk of steps each lasting $\sim 1/\omega$ and of size which is enhanced by an amount $\underline{E}$. This is equivalent to an enhanced diffusivity $\tilde{\underline{D}}$ which depends only on λ; this is an entirely nonlinear effect (the linear term in λ vanishes). Thus the flow need not be "strong" in any sense to observe enhancement effects; all that is needed is a large net strain in one cycle as parametrized by λ. The microscopic-macroscopic interaction gives rise to a pseudoequilibrium behavior in which position fluctuations grow diffusively as without flow but with a modified diffusivity which is accessible in straightforward experiments.

Superposed on these fluctuations in particle position (which determine how a cloud disperses) is the pure deterministic affine displacement (which is the true displacement for a fluid element). In order of magnitude this contribution equals the size of the system and depends multiplicatively on the initial macroscopic position. As far as the microscopic analysis is concerned this is therefore an infinite term, depending on the particular manner in which the system is set up, which must be subtracted off to leave behind a well-defined system-independent expression for the fluctuations. The small-time (relative to the flow period) displacement is characterized by equilibrium fluctuations plus a linear deterministic term. This latter term is still "infinite."

In Secs. III–V we asked what happens when the ω blob and Ω blob enter the τ_0^{-1} blot, Fig. 6(c). Now the internal degrees of freedom are excited and the results of course depend on the specific internal properties of the particle; we considered a simple polymer model, the Rouse model, as an example of a particle with an infinite number of such modes. For large polymer scales we found both the polymer statics and dynamics are enhanced by the same tensor $\underline{E}(\lambda)$ which enhanced the center-of-gravity motion. Now the affine flow operator $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_t^T$ which describes equal time separations and periodically deforms the chain of enhanced size is the same as the affine operator which appeared in the center-of-gravity problem. This reflects the physical fact that the center-of-gravity result describes a cloud of diffusing particles which gets periodically deformed, just like the polymer. However, the enhanced chain unit fluctuations [see Eq. (65)] are operatored on by $\underline{\Gamma}_t\{\cdots\}\underline{\Gamma}_{t_0}^T$ which is subtly different and drives from the fact that the initial state of the polymer (as determined by the value of the phase ωt_0) is never forgotten by the fluctuations in the *displacement* of the chain unit over some interval in time. The displacement involves the state of the chain both at time t and at time t_0, and thus its statistical properties depend on the initial phase no matter how large the time interval may be. Thus the fluctuation in displacement will be quite different if the initial state is, say, a compressed one (in which fluctuations in chain unit position are relatively small) as opposed to a strongly stretched one (fluctuations in position spread out over a larger volume). This effect is of course entirely absent when time translational invariance (broken here by the flow) pertains in which case the probability distribution describing the chain at some instant is independent of time after an initial transient (while here it is periodic).

The essence of the polymer large scales was an underlying reversible process (the **x** oscillators) which gave rise to statistics and dynamical fluctuations as in equilibrium but enhanced. For both center-of-gravity and internal modes, large scales are in "pseudoequilibrium." The flow breaks time translational and reversal invariance (which is the characteristic of the equilibrium state); however, on time scales large compared to the flow period these are recovered in an "enhanced form" where the nature of the

enhancement depends on the details of what happens in one flow cycle.

Similarly to the center of gravity motion there are, superposed on the enhanced pseudoequilibrium fluctuations, certain deterministic motions suffered by a chain unit. There is the deterministic part of the center-of-gravity motion with which the chain unit moves of course; this is one "infinity." But now there is another interesting and "infinite" affine term (we called it the "elastic band" term) which arises because the unit is attached to a chain which oscillates deterministically in the flow. This produces motions of the order of the size of the polymer chain itself. As for the center of gravity, one must carefully subtract off both "infinite" terms when dealing with the modes; only then does one recover "good" finite system-independent expressions for the local fluctuations. The process is somewhat reminiscent of renormalization techniques used in various branches of physics [49,50].

For short times relative to the flow period, fluctuations in chain unit position are as in equilibrium ($\underline{D}$, not $\tilde{\underline{D}}$). However, the two kinds of deterministic terms mentioned above are still important. Both are linear in time.

It is natural to ask, why are the enhancements characterizing chain unit diffusivity $\tilde{\underline{D}}$ and the polymer size identical? We can understand this as follows. $\tilde{\underline{D}}$ determines how fluctuations in chain unit position increase with time, i.e., it dictates how quickly the polymer loses memory of a configuration. Thus the usual relation still holds for quantities with tildes: $\tilde{\underline{D}} \approx \tilde{\mathbf{R}}^2/\tilde{\tau}_0$ where $\tilde{\mathbf{R}}^2$ and $\tilde{\tau}_0$ are, respectively, the enhanced mean-square size and relaxation time of the chain in the periodic flow. But for the Rouse model $\tilde{\tau}_0 = \tau_0$, i.e., the relaxation time of the chain is unchanged by the stretching effect of the flow. This is a pathology of Rouse dynamics and arises because information is communicated along the backbone only so relaxation times are dictated by numbers of chain units alone. Therefore $\tilde{\underline{D}} \approx \tilde{\mathbf{R}}^2/\tau_0$. But since $\underline{D} \approx \mathbf{R}^2/\tau_0$, it follows that the relation between $\tilde{\underline{D}}$ and $\underline{D}$ and that between $\tilde{\mathbf{R}}^2$ and $\mathbf{R}^2$ must be the same, i.e., the enhancements of spatial extension and diffusivity must be identical.

Of course, the relation $\tilde{\underline{D}} \approx \tilde{\mathbf{R}}^2/\tilde{\tau}_0$ is another way of saying that the center-of-gravity diffusivity and the diffusivity characterizing a single chain unit (for large times) are one and the same thing. Therefore the argument above explains why the center-of-gravity diffusivity is enhanced identically to the polymer size *when the ω blob and Ω blob lie inside the τ_0^{-1} blob.* However, it does not answer the following question: why does $\underline{E}(\lambda)$ have the same functional form for center-of-gravity diffusion when the flow blobs are far *outside* the polymer blob as it has when the flow blobs are far *inside* the polymer blob? The reason is the pathology of the Rouse model mentioned above; the center-of-gravity zeroth mode decouples from the others and so always obeys the same equation regardless of what the internal modes may be doing. In a more realistic model this feature will not survive of course. The form of $\underline{E}(\lambda)$ will remain as derived in this paper for flow blobs far outside the polymer blob, Figs. 6(a) and 6(b). However, as the flow blobs pass into the polymer blobs [as in Fig. 6(c)] the λ dependence of $\underline{E}$ will cross over to some quite different form.

Experimentally, the results in this study are directly relevant to dilute solutions when flow frequencies are much less than internal relaxation times. When these frequencies are large compared to internal frequencies, our analysis deals with the case when the particles are polymer molecules. A number of important physical effects are missing from our description of the polymer physics in this regime: excluded volume and hydrodynamical interactions [19] and, in some regimes, finite extensibility effects. These latter result when a polymer becomes so stretched in a flow that the rigidity of the backbone comes into play, i.e., the restoring force ceases to be quadratic (Gaussian model) and begins to saturate [27]. Such effects are important if λ is very large compared to unity. But if λ is of order unity the Gaussian model is still applicable since the total stretch (embodied in the enhancement tensor) depends on λ only. In a more complex model one expects a number of physical effects to survive, in particular the existence of an enhancement $\underline{E}$ albeit with a form which changes as one "enters" the τ_0^{-1} blob as discussed above.

The simplest and most interesting experiments suggested by the present work are therefore the measurements of enhanced diffusivity as a function of λ into the nonlinear regime. The periodicity of the flow provides a number of advantages for experiments on polymeric systems. In periodic flows there are none of the difficulties, which plague time-independent flow experiments, in contriving that a polymer chain be subjected to shear for a sufficiently long period to substantially affect it; a chain is constantly and automatically reinjected into the stretching region when the flow is periodic. Furthermore, one now has the ability to observe nonlinear effects in a controlled manner; since the flow does not continue to stretch a chain indefinitely, there are no "runaway" effects which (while intrinsically interesting) complicate interpretation since standard polymer models presumably break down at that point. With the flows considered here one can have nonlinearity without runaway.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant No. CTS-89-08995.

APPENDIX A: THE CASE OF NONVANISHING VELOCITY-GRADIENT TIME AVERAGE

In Sec. II it was stated that when the mean of $\Omega(t)$ is finite the limit defining $\tilde{\underline{D}}$ no longer exists and qualitatively different behavior prevails. Here we justify this. The new behavior depends on which of three classes of matrix $\underline{A}$ belongs to; we consider each class in turn below. Define $\underline{B} \equiv f(t)\underline{A}$ where $f(t) \equiv -\int_0^t \Omega(t')$, so the enhancement tensor is written $\underline{E} = \langle \exp(\underline{B}) \exp(\underline{B}^T) \rangle_t$. Thus finite mean velocity gradient means that $f(t)$ grows like t for large times.

1. $\underline{A}$ has only vanishing eigenvalues

An example belonging to this class is shear flow [Eq. (5)]. Generally one can express $\underline{A}$ in Jordan canonical

form [see the discussion following Eq. (36)] as $\underline{A}=\underline{P}(\Lambda+\underline{N})\underline{P}^{-1}$ where $\underline{P}$ is a nonsingular transformation into the canonical frame, Λ is the diagonal matrix of the eigenvalues of $\underline{A}$, and $\underline{N}$ is nilpotent ($\underline{N}^m=\underline{0}$ for some m less than or equal to the number of rows in $\underline{A}$, i.e., the dimension of space). In the present case the diagonal matrix Λ vanishes. Then $\exp(\underline{B})=\exp[f(t)\underline{A}]=\exp[f(t)\underline{I}\,\underline{P}\,\underline{N}\,\underline{P}^{-1}]=\underline{P}\exp[f(t)\underline{N}]\underline{P}^{-1}$. By expanding in powers of $f(t)\underline{N}$, it therefore follows that $\mathrm{tr}[\exp(\underline{B})\exp(\underline{B}^T)]$ is a polynomial in $f(t)$, i.e., for large times a polynomial in t if $f(t)$ has a linear part in t. But expanding $\exp(f\underline{A})\exp(f\underline{A}^T)$ to second order in $\underline{A}$ one sees that the trace must be at least second order in f since $\mathrm{tr}\underline{A}\,\underline{A}^T>0$.

The conclusion for this case is that when the flow field has nonvanishing mean the time integral of $\exp(\underline{B})\exp(\underline{B}^T)$ grows asymptotically at least quadratically in time in a manner completely determined by the mean velocity gradient [i.e., the linear term in $f(t)$]. Thus $\underline{E}$ does not exist and the fluctuation in particle position [see Eq. (11)] grows as a polynomial in time whose leading behavior for large times is of quadratic or higher order.

2. $\underline{A}$ has pure imaginary nonvanishing eigenvalues

Here $\underline{A}$ is antisymmetric and represents pure rotational flow. Since $\underline{A}+\underline{A}^T=0$, the commutator $[\underline{B},\underline{B}^T]$ vanishes and thus $\exp(\underline{B})\exp(\underline{B}^T)=\exp(B+B^T)=\underline{I}$. There is no enhancement, in fact no interesting flow effects at all as one would expect from the rotational symmetry of the Langevin equation without flow.

3. $\underline{A}$ has at least one eigenvalue with nonvanishing real part

This is the "generic" case if one picks matrices $\underline{A}$ at random; $\underline{A}$ now has a nonzero symmetric part and its Jordan canonical form involves nonvanishing Λ with at least one element with *positive* real part (since the sum of the eigenvalues vanishes). Name the eigenvalues of $\underline{A}$ and the diagonal elements of $\exp(\underline{B})$ to be $\{\lambda_i\}$ and $\{u_i\}$, respectively, where i ranges from 1 to d (d being the dimension of space). Now since the trace of the product of a matrix with its transpose is equal to the sum of the squares of its elements one has

$$d\,\mathrm{tr}[\exp(\underline{B})\exp(\underline{B}^T)]\geq d\sum_{i=1}^{i=d}u_i^2\geq\left[\sum_{i=1}^{i=d}u_i\right]^2=[\mathrm{tr}\exp(\underline{B})]^2\,, \tag{A1}$$

where we have used the fact that the $\{u_i\}$ are real since $\underline{B}$ is real. The second inequality follows from the Cauchy-Schwarz inequality. Expressing $\underline{B}$ in Jordan canonical form, $\underline{B}=\underline{P}(\Lambda+\underline{N})\underline{P}^{-1}$, we have $\exp(\underline{B})=\underline{P}(\exp\Lambda\exp\underline{N})\underline{P}^{-1}$ since Λ and $\underline{N}$ commute. Thus $\mathrm{tr}\exp(\underline{B})=\mathrm{tr}[\exp(\Lambda)\exp(\underline{N})]=\mathrm{tr}[\exp\Lambda]$ since $\exp(\underline{N})$, being a polynomial in $\underline{N}$, has diagonal elements equal to unity because any positive power of $\underline{N}$ has vanishing diagonal elements. Now since the eigenvalues of $\underline{B}$ equal $f(t)$ times those of $\underline{A}$, this latter expressions is a sum of terms of the form $\exp[f(t)\lambda_i]$. Therefore if $f(t)$ has a linear part this expression grows exponentially in time for large t since at least one of the λ_i has positive real part. From Eq. (A1) this implies that the same is true of $\mathrm{tr}[\exp(\underline{B})\exp(\underline{B}^T)]$ and thus $\underline{E}$ is not defined.

In conclusion, for a "generic" flow matrix $\underline{A}$, if the flow field has nonvanishing mean the time integral of $\exp(\underline{B})\exp(\underline{B}^T)$ grows asymptotically exponentially in time in a manner again completely determined by the mean velocity gradient. The fluctuation in particle position therefore also grows exponentially with time.

APPENDIX B: SMALL CONTRIBUTIONS TO AFFINE SCALES FROM LARGE p MODES

In Secs. III and IV we calculated dynamical and static quantities pertaining to long times (relative to $1/\omega$) and large length scales [relative to the size of the "ω blob" comprising s_ω chain units introduced following Eq. (58)]. These are the scales where the behavior turns out to be "affine" deformation in the flow plus fluctuations, and in deriving our results the affine form of the mode correlation functions, Eq. (57), was used for *all* p values. But $p>p_\omega$ [see Eq. (58)] modes do not actually obey this affine result. To obtain the error following from the affine assumption on these large p modes, let us assume that $\lambda=O(1)$. Then the exact mode correlation function and the affine form for the same p value are of the same order of magnitude (since the elements of $\underline{\Gamma}_t$ are then of order unity). Therefore if we can demonstrate that $p>p_\omega$ is an unimportant band in the calculations based on the assumption that all modes are affine, we have justified our procedure in Secs. III and IV. But the affine mode correlation equals the equilibrium value operated on by $\underline{\Gamma}_t\underline{E}\,\underline{\Gamma}_{t_0}^T$; thus the task reduces simply to examining the role of $p>p_\omega$ modes in the calculation of correlation functions for a Rouse chain in the absence of flow. The relative corrections will be of the same order of magnitude as in our approximation scheme.

The most general quantity is that involved in the coherent scattering function, which we express in terms of modes as follows:

$$\begin{aligned}\langle[\mathbf{u}(s+s',t+t')-\mathbf{u}(s',t')]^2\rangle^{\mathrm{eq}}&=\frac{2}{N}\sum_{p=1}^{\infty}\left\langle\left[\mathbf{r}_p(t+t')\cos\frac{p\pi(s+s')}{N}-\mathbf{r}_p(t')\cos\frac{p\pi s'}{N}\right]^2\right\rangle^{\mathrm{eq}}\\&\approx\int_{1/N}^{\infty}dq\,\langle\mathbf{r}_q^2\rangle^{\mathrm{eq}}\left[1-\cos qs\frac{\langle\mathbf{r}_q(t)\mathbf{r}_q(0)\rangle^{\mathrm{eq}}}{\langle\mathbf{r}_q^2\rangle^{\mathrm{eq}}}\right]\\&\approx\mathrm{Re}\int_0^{\infty}dq\frac{1}{q^2}[1-\exp\{iqs-q^2t/\zeta\}]\,.\end{aligned} \tag{B1}$$

Here $\mathbf{u}(s,t)$ is the position relative to the center of gravity, and the sum over p can be read off from Eq. (72). We have run the sum into an integral over q with $q=p\pi/N$ and ignored numerical prefactors in the above. The relative chain coordinate s is finite, and absolute coordinate s' is "infinite" (i.e., well inside the polymer) such that $qs' \gg 1$ for almost all of the q integration range which causes several rapidly oscillating cosines to vanish approximately.

We want to show that if we replace the upper q limit by $1/s_\omega \equiv N/p_\omega = N/(\omega\tau_0)^{1/2}$ the error is small when s,t belong to "affine" scales, i.e., $s \gg s_\omega, t \gg 1/\omega$. But when these last inequalities are true then in the correlation term, namely, the integral form $1/s_\omega$ to ∞, there is negligible contribution from the exponential term since $t/(s_\omega^2\zeta)=\omega t \gg 1$ and $s/s_\omega \gg 1$. Thus one has

$$\frac{\mathrm{Re}\int_{1/s_\omega}^{\infty} dq(1/q^2)[1-\exp\{iqs-q^2t/\zeta\}]}{\mathrm{Re}\int_0^{\infty} dq(1/q^2)[1-\exp\{iqs-q^2t/\zeta\}]} \approx \frac{s_\omega}{s+(t/\zeta)^{1/2}f(s^2\zeta/t)}$$

$$= \frac{1}{s/s_\omega+(\omega t)^{1/2}f(s^2\zeta/t)} \ll 1 \ . \tag{B2}$$

The denominator was obtained from Eq. (74) (with flow set to zero); f is of order unity in general, depending on the ratio $s^2\zeta/t$. Evidently the errors are very small provided we always deal with scales much larger than those characterizing the "ω blob." Note that the quantities required for the mean-square displacement of a chain unit and for the mean separation of two chain units are special cases in which $s=0$, $t=0$, respectively.

For larger values of λ the discussion is more complex since one must compare the above small factors to large elements of $\underline{\Gamma}_t$. However, one may still say that for any value of λ there exists a value of N such that if the number of chain units exceeds this value then the affine approximation is valid.

[1] G. Taylor, Proc. R. Soc. London, Ser. A **219**, 186 (1953).
[2] P. E. Rouse, J. Chem. Phys. **21**, 1272 (1953).
[3] B. O'Shaughnessy, C. Durning, and M. Tabor, J. Chem. Phys. **92**, 2637 (1989).
[4] J. L. Lumley, Annu. Rev. Fluid Mech. **1969**, 367.
[5] J. L. Lumley, J. Polym. Sci. Macromol. Rev. **7**, 263 (1973).
[6] M. Tabor and P. G. de Gennes, Europhys. Lett. **2**, 9 (1986).
[7] P. G. de Gennes, Physica (The Hague) A **140**, 9 (1986).
[8] G. Ryskin, Phys. Rev. Lett. **59**, 2059 (1987).
[9] Q. Xia, H. D. Ou-Yang, D. J. Pine, and P. M. Chaikin, Phys. Rev. Lett. **61**, 2554 (1988).
[10] T. Hirosye, Y. Einaga, and H. Fujita, Polymer **11**, 819 (1979).
[11] Y. Miyaki, Y. Einaga, T. Hirosye, and H. Fujita, Macromolecules **10**, 1356 (1977).
[12] B. Zimm, Macromolecules **13**, 592 (1980).
[13] J. G. de la Torre, A. Jimenez, and J. J. Freire, Macromolecules **15**, 148 (1982).
[14] J. D. Ferry, *Viscoelastic Properties of Polymers,* 3rd ed. (Wiley, New York, 1980).
[15] K. Osaki, Adv. Polym. Sci. **12**, 1 (1973).
[16] D. W. Hair and E. J. Amis, Macromolecules **22**, 4528 (1989).
[17] D. W. Hair and E. J. Amis, Macromolecules **23**, 1889 (1989).
[18] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[19] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1985).
[20] J. G. Kirkwood and J. Riseman, J. Chem. Phys. **16**, 565 (1948).
[21] Y. Oono, J. Chem. Phys. **79**, 4629 (4629).
[22] A. Jaganathan, Y. Oono, and B. Schaub, J. Chem. Phys. **86**, 2276 (1987).
[23] F. C. Frank and M. R. Mackley, J. Polym. Sci. **14**, 1121 (1976).
[24] G. G. Fuller and L. G. Leal, Rheol. Acta **19**, 580 (1980).
[25] I. Noda, Y. Yamada, and M. Nagasawa, J. Phys. Chem. **72**, 2890 (1968).
[26] P. R. Williams and R. W. Williams, J. Non-Newtonian Fluid Mech. **19**, 53 (1985).
[27] P. G. de Gennes, J. Chem. Phys. **60**, 5030 (1979).
[28] M. Fixman, J. Chem. Phys. **45**, 785 (1966); **45**, 793 (1966).
[29] H. C. Ottinger, J. Chem. Phys. **86**, 3731 (1987).
[30] Y. Rabin and K. Kawasaki, Phys. Rev. Lett. **62**, 2281 (1989).
[31] Y. Rabin, H. C. Ottinger, and K. Kawasaki, in *Macromolecular Liquids,* edited by C. R. Safinya, S. A. Safran, and P. A. Pincus MRS Symposia Proceedings No. 176 (Materials Research Society, Pittsburgh, 1990).
[32] Y. Rabin and H. C. Ottinger, Europhys. Lett. **13**, 423 (1990).
[33] P. R. Baldwin and E. Helfand, Phys. Rev. A **41**, 6772 (1990).
[34] C. C. Han and A. Z. Akcasu, Macromolecules **14**, 1080 (1981).
[35] Y. Tsunashima, N. Nemoto, and M. Kurata, Macromolecules **16**, 584 (1983).
[36] Y. Tsunashima, M. Hirata, N. Nemoto, K. Kajiwara, and M. Kurata, Macromolecules **20**, 2862 (1987).
[37] G. Allan, R. Ghosh, J. S. Higgins, J. P. Cotton, B. Farnoux, G. Jannink, and G. Weill, Chem. Phys. Lett. **38**, 577 (1976).
[38] Z. Akcasu and J. S. Higgins, J. Polym. Sci. **15**, 1745 (1977).
[39] D. Richter, J. B. Hayter, F. Mezei, and B. Ewen, Phys. Rev. Lett. **41**, 1484 (1978).
[40] L. K. Nicholson, J. S. Higgins, and J. B. Hayter, Macromolecules **14**, 836 (1981).
[41] F. R. Cottrell, E. W. Merill, and K. A. Smith, J. Polym. Sci. Part A 2 **7**, 1415 (1969).
[42] P. Lindner and R. C. Oberthur, Colloid Polym. Science

263, 443 (1985).
[43] P. Lindner and R. C. Oberthur, Colloid Polym. Science **266**, 866 (1988).
[44] A. W. Marshall and I. Olkin, *Inequalities: Theory of Majorization and Its Applications* (Academic, New York, 1979).
[45] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
[46] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1970).
[47] Seymour Lipchutz, *Linear Algebra* (McGraw-Hill, New York, 1974).
[48] P. G. de Gennes, Physics (Long Island City, N.Y.) **3**, 37 (1967).
[49] D. J. Amit, *Field Theory, the Renormalization Group, and Critical Phenomena* (World Scientific, Singapore, 1984).
[50] G. K. Batchelor, J. Fluid. Mech. **52**, 245 (1972).