# Soft Matter

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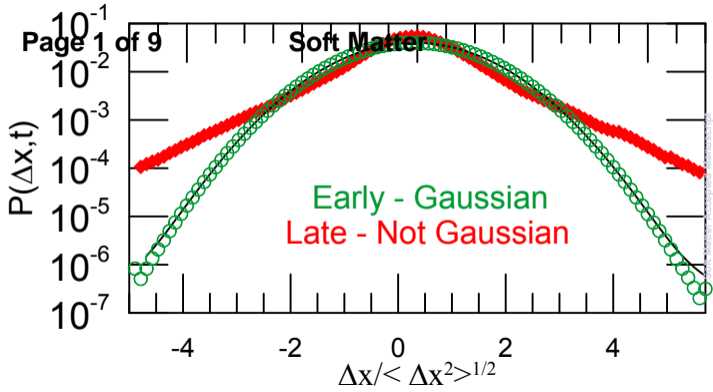
In complex fluids the Gaussian Diffusion Approximation is generally invalid

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The Gaussian Diffusion Approximation proposes that the distribution of displacements Δx for a particle diffusing through a complex fluid has a Gaussian dependence on Δx. We demonstrate from experimental evidence and computer simulations that this approximation is generally incorrect in complex fluids. As a result, experimental studies that have used the Gaussian Diffusion Approximation to interpret their findings will need to be reconsidered.

1 Introduction

The Gaussian Diffusion Approximation was introduced a century ago to treat Brownian motion and diffusion by mesoscopic particles and dilute neutral solutes in low-viscosity liquids. Within the limits of then-current experimental instrumentation, the approximation was adequate for its intended purpose: It gave a reasonable microscopic description of diffusion in simple systems. Under modern conditions, diffusion measurements in complex fluids are often used to study the complex fluid's dynamics. The Gaussian Diffusion Approximation is then sometimes applied to these measurements, e. g., to infer mean-square particle displacements.

The thesis of this paper is that many modern invocations of the Gaussian Diffusion Approximation in soft matter studies have taken the approximation entirely outside its range of validity. In consequence, inferences based on the approximation can be seriously misleading. Conversely, predictions of diffusive behavior based on molecular models and the Gaussian Diffusion Approximation may be significantly in error, even though the molecular models are entirely adequate.

The Gaussian Diffusion Approximation, written for motion along one coordinate axis, provides[1,2]

$$P(\Delta x, t) = \frac{\exp(-(\Delta x)^2/(2\langle(\Delta x(t))^2\rangle))}{(2\pi\langle(\Delta x(t))^2\rangle)^{0.5}}. \qquad (1)$$

Here $P(\Delta x, t)$ is the probability of observing a displacement Δx of a diffusing particle during a time interval t. $P(\Delta x, t)$ is sometimes known as the van Hove function. The mean-square displacement of the diffusing particle during time t enters the van Hove function via the factor $\langle(\Delta x(t))^2\rangle$ in the exponential.

An incomplete list of experimental techniques whose outcomes are sometimes interpreted by invoking this approximation includes (i) pulsed field gradient nuclear magnetic resonance using the Stejskal-Tanner equation, (ii) particle tracking microrheology, (iii) fluorescence correlation spectroscopy, (iv) diffusing wave spectroscopy, (v) fluorescence photobleaching recovery, (vi) x-ray correlation spectroscopy, (vii) optical particle tracking, (viii) inelastic neutron scattering, and (ix) optical probe diffusion/microrheology. Our own interest in these techniques traces back to a long-ago series of papers by Hallet and students[3,4], who introduced the idea of studying polymer solution dynamics by using quasielastic light scattering to observe the diffusion of dilute polystyrene spheres through solutions of weakly-scattering polymers.

In saying that the combination of any of these techniques with the Gaussian approximation may lead to difficulties, we emphasize: (i) The literal experimental data are not in question, only their interpretations; and (ii) Control experiments that validated these techniques in simple Newtonian fluids are not relevant for the discussion here.

To understand why the Gaussian approximation is invoked so frequently, it is worthwhile to begin with the theoretical rationale for using it. The rationale is based on the Central Limit Theorem. The qualitative notion is that diffusive motion can be envisioned as occurring because the diffusing particle takes large numbers of random steps. Except over very short times, sequential steps are said to be independent (uncorrelated). In an equilibrium system, the distribution functions for all the random steps are said to be the same. If these conditions are satisfied, the Central Limit Theorem says that a sum Δx of a large number of very small random steps must have the Gaussian distribution seen in Eq. 1. Of course, the claim that sequential diffusive steps are uncorrelated must face the challenge that this claim is already known to be invalid in simple and glassy liquids[5–7]. In simple liquids, particle displacements remain correlated over long times due to the long-time persistence of hydrodynamic forces, the 'hydrodynamic

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tail', as has been observed experimentally by Boon and by Bouiller[8,9]. Nonetheless, Gaussian diffusion appears attractive as an approximation to real diffusion.

The reason that the Gaussian Diffusion Approximation must be viewed as highly suspect in complex fluids is a second mathematical result, namely Doob's Theorem[10]. For the trajectory of a diffusing particle, the conditions under which Doob's Theorem is applicable are precisely the same as the conditions under which the Central Limit Theorem is applicable. If one theorem is applicable, so must be the other. Doob's Theorem constrains the time dependence of Δx. Whenever particle motions lead via the Central Limit Theorem to the Gaussian of Eq. 1, it is necessarily the case from Doob's Theorem that the mean-square particle displacement increases linearly with time, namely

$$\langle (\Delta x(t))^2 \rangle = 2Dt. \qquad (2)$$

The diffusion coefficient D of Doob's Theorem is a time-independent constant. However, in complex fluids many experiments are not consistent with Eq. 2. If Doob's Theorem does not describe some system, then the Central Limit Theorem also cannot describe that system, so therefore experiment is also not consistent with using the Central Limit Theorem to describe single-molecule diffusion in that system.

Our result on the Gaussian Diffusion Approximation in complex fluids has substantial antecedents in other systems. It has long been known for simple liquids that the Gaussian Diffusion Approximation is invalid on short time scales[5,6]. In small-molecule single-component liquids at short times, the van Hove function $P(\Delta x, t)$ is not a Gaussian in Δx. Furthermore, in the same fluids $\langle (\Delta x(t))^2 \rangle$ does not increase linearly with t. On the same line, it is well-established that solution dynamics in glass-forming fluids close to the glass transition is characterized by several universal features, including stretched-exponential-in time relaxations and van Hove functions having fat exponential tails.[7] These features show that the Central Limit Theorem does not describe molecular motion in near-glass liquids. However, the complex fluid community has not uniformly recognized the significance of these well-established simple-liquid behaviors for studies of complex fluids, as witness the community's widespread invocation of the Gaussian Diffusion Approximation.

The following Sections of this paper present extensive evidence that the Gaussian Diffusion Approximation should not be invoked in complex fluid studies. Section 2 presents experimental evidence already found in the literature showing that the approximation is invalid. Section 3 develops a series of computer simulations of Gaussian and non-Gaussian random walks. Section 4 presents outcomes of the simulations, showing that when non-Gaussian random walks are interpreted by applying the Gaussian Diffusion Approximation, substantial errors arise. Section 5 offers a discussion of our findings.

2 Experimental Evidence

This Section notes five sorts of experimental data showing that the Gaussian Diffusion Approximation is invalid in complex fluids. There are direct experimental tests of Eq. 1, direct experimental tests of equation 2, and three classes of experiment that address the spatial Fourier transform $g^{(1s)}(q,t)$ of $P(\Delta x, t)$.

First, $P(\Delta x, t)$ has been measured directly with particle tracking. Early measurements of $P(\Delta x, t)$ by Apgar, et al.[11] and Tseng, et al.[12] clearly revealed non-Gaussian forms for $P(\Delta x, t)$. More recent studies by Wang, et al.[13,14], and Guan, et al.[15], the last being measurements on a near-ideal system of colloidal hard spheres diffusing through nondilute suspensions of larger hard spheres, confirmed a non-Gaussian distribution of $P(\Delta x, t)$. The more recent studies reveal the form of the distribution, namely $P(\Delta x, t)$ is nearly Gaussian for smaller $|\Delta x|$, but, at larger $|\Delta x|$, $P(\Delta x, t)$ decreases approximately exponentially in $|\Delta x|$. These are the 'fat tails' described by Chaudhuri, et al.[7] for glassy systems. By direct measurement, $P(\Delta x, t)$ in complex fluids is thus not a Gaussian in Δx.

Second, $\langle (\Delta x(t))^2 \rangle$ has been measured using particle tracking. In some systems, experiment finds

$$\langle (\Delta x(t))^2 \rangle = at^\alpha \qquad (3)$$

for a a constant and $\alpha < 1$, the case termed *subdiffusion*. Experimental studies reporting subdiffusion were reviewed by Saxton[16]. Doob's Theorem shows: If the Gaussian Diffusion Approximation based on the Central Limit Theorem is valid in a system, then it is mathematically impossible for subdiffusive behavior to be observed; in Gaussian diffusive systems, $\alpha = 1$ must be obtained. If $\alpha \neq 1$, then the system cannot be Gaussian.

Finally, quasielastic light scattering has been used to study optical probe diffusion through complex fluids. Optical probe diffusion is applicable to complex fluids that scatter light weakly. In an optical probe experiment, one observes the motions of a dilute suspension of intensely-scattering optical probes through a complex fluid matrix. For a successful experiment, either the probes completely dominate scattering by the complex fluid of interest, or the spectra of the probes has been purified of scattering by the complex fluid spectrum via subtraction at the field correlation function level. In a probe experiment, quasielastic light scattering measures directly the spatial Fourier transform of P, namely

$$g^{(1s)}(q,t) = \int_{-\infty}^{\infty} d\Delta x \, P(\Delta x, t) \exp(iq\Delta x). \qquad (4)$$

Up to a possible normalizing constant, $g^{(1s)}(q,t)$ is the self part of the probe dynamic structure factor, with q being the scattering vector, the self part being observed because the probes are dilute.

In systems that are described accurately by the Gaussian Diffusion Approximation, eq 4 becomes

$$g^{(1s)}(q,t) = \exp(-q^2 \langle (\Delta x(t))^2 \rangle / 2), \qquad (5)$$

and on applying Doob's Theorem

$$g^{(1s)}(q,t) = \exp(-Dq^2 t). \qquad (6)$$

Eq 5 is sometimes interpreted as showing that $\langle (\Delta x(t))^2 \rangle$ can be obtained from $g^{(1s)}(q,t)$ in non-trivial cases. Eq. 6 shows that if the Gaussian Diffusion Approximation is applicable then $g^{(1s)}(q,t)$ must necessarily be a simple exponential in t and in q^2.

Light scattering studies of probe diffusion readily identify systems in which Eq. 6 is incorrect. In some systems, the time dependence is wrong. Strelezky and Phillies[17] report systems in which $g^{(1s)}(q,t)$ relaxes as a stretched exponential $\exp(-\theta t^\beta)$ in time, θ and β being line shape parameters, with $\beta \neq 1$. In other systems, $g^{(1s)}(q,t)$ gains multiple relaxations on different time scales[18–20]. In yet other systems, the q^2 dependence is wrong. Several authors[18–21] report cases in which the relaxation $\log(g^{(1s)}(q,t))$ is not linear in q^2. From the spatial Fourier transform relation, if $\log(g^{(1s)}(q,t))$ is not linear in q^2, $P(\Delta x,t)$ can not be a Gaussian in Δx. In all these systems, the Gaussian Diffusion Approximation cannot possibly be correct, because $g^{(1s)}(q,t)$ does not have the properties required for Gaussian diffusers by the Central Limit Theorem and Doob's Theorem.

The above are five lines of experimental evidence showing that the Gaussian Diffusion Approximation is not valid in many complex fluids. In particular, we have considered (i) direct measurement of $P(\Delta x,t)$, (ii) direct measurement of $\langle (x(t))^2 \rangle$, (iii) the time dependence of $g^{(1s)}(q,t)$, (iv) multimodal lineshapes of $g^{(1s)}(q,t)$, and (v) direct measurement of the q-dependence of $g^{(1s)}(q,t)$.

3 Simulations

As a further demonstration that the Gaussian Diffusion Approximation is invalid in complex fluids, we did computer simulations. Full details are in the Electronic Supplement. The simulations had two distinct parts. First, we generated trajectories $u(t)$ and $x(t)$ for the particle's velocity and position. Second, we generated statistical characterizations of particle motions.

A starting point for simulations is the Langevin equation

$$m\frac{du(t)}{dt} = -f_o u(t) + \mathscr{F}(t), \qquad (7)$$

which is a heuristic approximation introduced a century ago as a description of the diffusion of mesoscopic particles in simple fluids. In this equation, $u(t)$ is the time-dependent particle velocity, m and f_o are the probe's mass and drag coefficient, and $\mathscr{F}(t)$ is the thermal "random" force on the particle. f_o and $\mathscr{F}(t)$ are interlinked by the fluctuation-dissipation theorem. The thermal force is taken to have a very short correlation time, so that impulses $\int \mathscr{F}(t)dt$ supplied to the particle by the fluid, over nonoverlapping time intervals, are very nearly independent from each other.

We first implemented Eq. 7 as a numerical simulation. $\mathscr{F}(t)$ was created with a pseudorandom number generator having a Gaussian distribution. We confirmed that $x(t)$ from our simulation has the properties expected[2] for a solution to the Langevin equation. In particular, we found a Gaussian distribution for $P(\Delta x,t)$, with a mean-square displacement that increases linearly with t.

To reveal non-Gaussian behavior, we used a more physically realistic form for the equation of motion. Our starting point was the Mori equation[22], which provides

$$m\frac{du(t)}{dt} = i\Omega u(t) - \int_{-\infty}^{t} ds\phi(t-s)u(s) + F^P(t). \qquad (8)$$

The Mori equation is a clever and complex rearrangement of Newton's Second Law, written as the Liouville equation. Here $u(t)$ is the dynamic variable of interest, in this work the probe velocity. For our systems Ω vanishes. $F^P(t)$ is the projected force; Mori's treatment gives an exact albeit formal expression for $F^P(t)$. The Mori memory kernel $\phi(s)$ is determined by the projected force, namely

$$\phi(s) = \langle F^P(0)F^P(s) \rangle / \langle (u(0))^2 \rangle. \qquad (9)$$

The Mori equation looks a great deal like the Langevin equation. However, the Langevin equation is a heuristic approximant. The Mori equation is an exact result of classical and statistical mechanics.

In applications of the Mori equation, the projected force $F^P(t)$ is often approximated as having a correlation time short compared to the time scales of interest. With this approximation, $\phi(s)$ is very nearly a delta function in time. For probes in complex fluids, this approximation loses the interesting physics. The central rationale for observing probe diffusion in complex fluids is to extract information about the relaxations of the complex fluids. To do so, probe motions must be observed on the time scales on which relaxations occur. On these time scales, $F^P(t)$ and $\phi(s)$ have prolonged correlations.

To apply the Mori equation, we needed an adequate model for a complex fluid. Our starting point is the observation that complex fluids have relaxations on multiple, very different time scales. For example, a probe particle diffusing in a polymer solution experiences fluctuating interactions with the solvent and largely independent fluctuating interactions with the polymer molecules. Corresponding to these two very different relaxations, the thermal driving force $F^P(t)$ and the effective

friction factor $\phi(s)$) should each be expected to have correlations and relaxations on multiple different time scales.

A model corresponding to these expectations has been developed by Tateishi, et al.[23]. Tateishi, et al., introduce an approximation to Eq. 8, in which $F^P(t)$ contains two uncorrelated noise sources $\xi(t)$ and $\eta(t)$. In Tateishi's calculation, the time correlation functions of $\xi(t)$ and $\eta(t)$ were a delta function and a power law. The corresponding memory kernel then had two components, namely

$$\phi(s) = \langle \xi(t)\xi(t+s) \rangle + \langle \eta(t)\eta(t+s) \rangle. \qquad (10)$$

It may appear somewhat obscure to say that the random force can be divided into two components. A recent physical model that displays this division explicitly is the *walking confined diffusion model* introduced by Ziebacz, et al.[24], and by Ochab-Marcinek and Holyst[25]. In this model, a probe in a polymer solution is said to be confined to a "cave", a spherical depletion zone centered on the probe from which the polymer is significantly excluded. Within the cave, the probe can diffuse relatively rapidly. The probe cannot move significantly beyond the edges of the depletion zone, because the viscosity outside the depletion zone is too large. However, the spherical depletion zone itself performs slow diffusion, taking the probe with it as it moves. The net result is that the probe particle performs motion on two different time and distance scales, a faster scale determined by the current location and size of the depletion zone, and a slower scale determined by the diffusion of the depletion zone. Correspondingly, the probe is subject to a rapidly fluctuating force that drives probe motion within the depletion zone, and a slowly fluctuating force corresponding to the gradual motion of the zone. A slightly different version of the model, in which the depletion zone perpetually relaxes via diffusion toward the current location of the probe, was provided by Phillies[26,27]; however, the interest in those papers was primarily the long-time behavior.

To implement the Tateishi, et al., calculation, we simulated a system with two random forces. The rapidly-fluctuating thermal force was represented by a random number generator giving a Gaussian-normal distribution output. The corresponding memory kernel was taken to be a delta function, giving the friction factor seen in the Langevin equation. To generate a second thermal force and memory kernel having the right long-time correlations, we used Mori's orthogonal hierarchy of thermal forces scheme[28]. The basis of the orthogonal hierarchy is Mori's observation that the time evolution of the projected thermal force can itself be calculated with a second Mori equation. We used the second Mori equation as a generalized Langevin equation to generate the needed random force, a force having the desired long-time correlations, and separately calculated the corresponding memory function $\phi(s)$, as discussed in the Supplemental Material. Mathemati-

cally, the long-lived projected force was constructed as a sum

$$F_i^P = \sum_{j=i-N}^{i} Y_j C_{i-j}. \qquad (11)$$

Here i and j label time steps in the calculation, while C_{i-j} propagates the contribution of the random source at time j forward to time i. N is the range of C_{i-j}, the largest value of $i-j$ for which a given Gaussian random variable Y_j contributes to F_i^P.

In our simulations, correlations in the slowly-relaxing fluctuations were chosen to relax exponentially with time. We also experimented with a projected force that had an exponential relaxation at short times and a power-law relaxation at longer times. This alternative projected force gives the same qualitative results as the results shown below for an exponential-correlated random force, so simulations using the alternative force were only used to confirm that our qualitative findings were not some quirk of an idiosyncratic choice of random forces.

We then generated an extensive set of characterizations of our trajectories $u(i)$ and $x(t)$ as obtained via numerical integration of our approximation to the Mori equation. Numerical integration gives the trajectories at equally spaced time steps; the natural time unit is a single time step. For each system we calculated the velocity-velocity correlation function

$$C_{VV}(t) = \langle u(0)u(t) \rangle, \qquad (12)$$

and the acceleration-acceleration correlation function

$$C_{AA}(t) = \langle (u(t_2) - u(t_1))(u(t_4) - u(t_3)) \rangle. \qquad (13)$$

$C_{AA}(t)$ was obtained for $t_1 \leq t_2 \leq t_3 \leq t_4$, with $t = t_3 - t_2$, while keeping $t_2 - t_1$ and $t_4 - t_3$ small.

The direct test of the displacement distribution function was the calculation of $P(\Delta x, t)$. Here $\Delta x(t) = x(\tau + t) - x(\tau)$. $P(\Delta x, 1)$ gives the distribution of $x(t) - x(t-1)$, which is also the distribution of $u(t)$. The $u(t)$ had the expected Gaussian distribution. $C_{VV}(t)$ is long lived, so errors due to time being discretized are small.

We calculated the time-dependent central moments $K_n(t)$ of $P(\Delta x, t)$ from the simple moments $\langle (\Delta x(t))^n \rangle$, namely

$$K_2(t) = \langle (\Delta x(t))^2 \rangle, \qquad (14)$$

$$K_4(t) = (\langle (\Delta x(t))^4 \rangle - 3(\langle (\Delta x(t))^2 \rangle)^2) / (\langle (\Delta x(t))^2 \rangle)^2, \qquad (15)$$

and

$$K_6(t) = (\langle (\Delta x(t))^6 \rangle - 15\langle (\Delta x(t))^4 \rangle \langle (\Delta x(t))^2 \rangle$$
$$+ 30\langle (\Delta x(t))^2 \rangle^3) / (\langle (\Delta x(t))^2 \rangle)^3. \qquad (16)$$

The odd central moments K_1, K_3, and K_5 of $P(\Delta x, t)$ were confirmed by direct calculation to vanish, as expected from

symmetry. In plotting $P(\Delta x, t)$, the abscissa was scaled by the root-mean-square displacement.

Many studies of the diffusion of probe molecules through complex fluids are based on scattering methods. These methods typically determine the intermediate scattering function

$$g^{(1s)}(q,t) = \langle \cos(q\Delta x(t)) \rangle. \quad (17)$$

We determined this function for wide ranges of q and t. As an indication of the simulation's accuracy, the relaxation of $g^{(1s)}(q,t)$ could generally be followed until $g^{(1s)}(q,t)/g^{(1s)}(q,0) < 3 \cdot 10^{-4}$, corresponding to a signal-to-noise ratio ca. 3000. It is sometimes assumed that $g^{(1s)}(q,t)$ is related to the mean-square displacement via

$$g^{(1s)}(q,t) = \exp(-q^2 \langle (\Delta x(t))^2 \rangle / 2). \quad (18)$$

We tested this hypothesis by plotting the directly-calculated (eq 17) and inferred (eq 18) values for $g^{(1s)}(q,t)$ against each other.

4 Results

We made extensive simulations on a probe that follows the Langevin equation and on a probe that follows the Mori equation with two driving forces. The Langevin simulation yielded all expected properties: $P(\Delta x, t)$ was a Gaussian at all times. Correspondingly, the higher central moments K_4 and K_6 of $P(\Delta x, t)$ were both very nearly zero at all times. $C_{VV}(t)$ relaxed exponentially in t. At times sufficiently long that $C_{VV}(t)$ had relaxed into the noise in the simulation, $\langle (\Delta x(t))^2 \rangle$ increased linearly with time. The intermediate scattering function $\log(g^{(1s)}(q,t))$ was linear in t, linear in q^2, and determined by $\langle (\Delta x(t))^2 \rangle$ via eq 18.

We now consider a diffusing probe in a complex fluid. The probe's diffusion was driven by two random forces, one being the Langevin driving force and the other having an exponential memory, and the two corresponding friction forces. The Langevin drag coefficient was $f_o = 0.1$. Our propagator was an exponential $C_i = f_1 \exp(-ai)/Q$ with $a = 0.01$, $f_1 = 0.1$, and normalization such that $\Sigma_i C_i = f_1$.

Figures 1 and 2 show important statistical properties of this probe. The velocity-velocity correlation function and mean-square displacement appear as Fig 1a. The time evolution of the mean-square displacement is undistinguished. The two solid lines represent the near-ballistic motion ($\langle (\Delta x(t))^2 \rangle \sim t^2$) at short times and pseudodiffusive motion ($\langle (\Delta x(t))^2 \rangle \sim t^1$) at long times. We say pseudodiffusive because $P(\Delta x, t)$ was not a Gaussian at long times. The time evolution of $\langle u(0)u(t) \rangle$ shows a perhaps-unexpected feature, namely an oscillation resembling a damped ringing motion. The oscillation is driven by the memory kernel, which creates a drag proportional to the velocity (the sequential displacements) at earlier times.
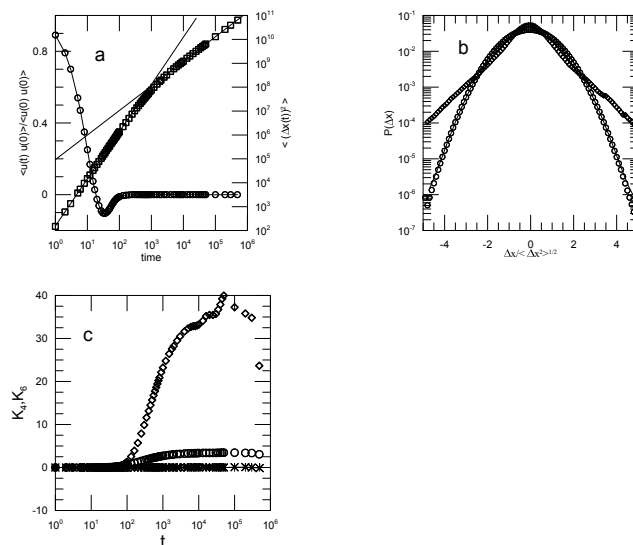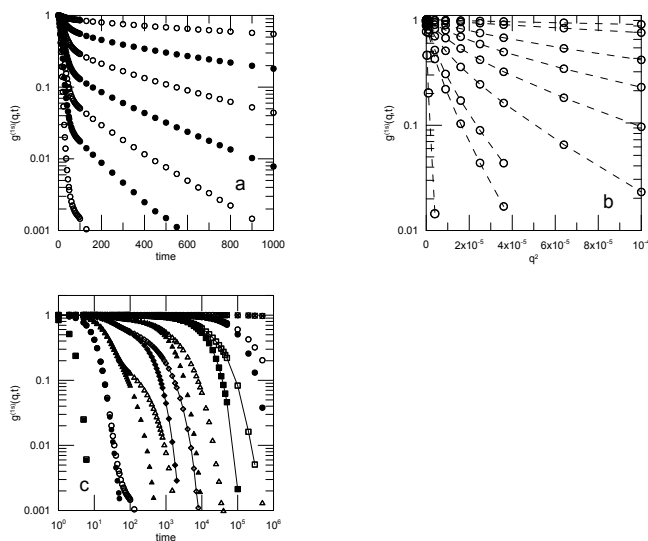

Fig. 1 Diffusion by a probe with a slow exponential memory. (a) $\langle v(0)v(t) \rangle / \langle (v(0))^2 \rangle$ (◯) and $\langle (\Delta x(t))^2 \rangle$ (□). (b) $P(\Delta x, t)$ at at 1 (◯) and 50,000 (◇) timesteps. (c) Cumulants K_4 and K_6 as functions of time for probes with a slow exponential memory (○, ◇, respectively) and for probes with a simple Langevin probe (+, ×, respectively).

Figure 1b shows $P(\Delta x, t)$ at short ($t = 1$) and long ($t = 50000$) times. The qualitative shape of $P(\Delta x, t)$ evolves in time. As seen in the figure, the short-time $P(\Delta x, 1)$ is a single Gaussian, measurements (points) matching a Gaussian fit (solid line). At the large time, $P(\Delta x, t)$ is not at all Gaussian. The central feature in $P(\Delta x, t)$, corresponding to $\Delta x / \langle (\Delta x(t))^2 \rangle^{1/2} < 1$ or so, is a central hump that could be approximated with a Gaussian. At larger Δx, $P(\Delta x, t)$ gains near-exponential wings, decreasing approximately as $\exp(-a|\Delta x|)$. Near-exponential wings have previously been found experimentally by Wang, et al. [13,14], and Guan, et al. [15].

Figure 1c shows the time dependence of the higher-order central moments of $P(\Delta x, t)$, both for the Langevin probe particle and also for the Mori-Zwanzig probe particle. For the Langevin probe, the higher-order cumulants are very nearly zero. For the Mori-Zwanzig probe, K_4 reaches a long-time asymptote, while K_6 also tends toward a fixed value. On the scale of Figure 1b, plots of $P(\Delta x, t)$ for the ten largest delay times are almost entirely indistinguishable; the apparent fluctuations in K_6 at these large times are seen because K_6 is a very small difference between extremely large numbers. There is clearly no tendency for $P(\Delta x, t)$ to return to Gaussian behavior, for which $K_4 = K_6 = 0$, at large times.

Figure 2a shows a semilog plot of the intermediate structure factor $g^{(1s)}(q,t)$ as a function of time for various values of q. The relaxation of $g^{(1s)}(q,t)$ is profoundly non-exponential,

Fig. 2 Diffusion by a probe with a slow exponential memory. (a) $g^{(1s)}(q,t)$ as a function of t for (from slowest to fastest decay) q of 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.08. (b) $g^{(1s)}(q,t)$ as a function of q^2 for (from slowest to fastest decay) t of 50, 300, 1800 4000, 8000, $1.6 \cdot 10^4$, $3.5 \cdot 10^4$, $5 \cdot 10^4$, and $4.9 \cdot 10^6$,(c) Comparison of $g^{(1s)}(q,t)$ (open points) and $\exp(-q^2\langle(\Delta x(t))^2\rangle/2)$ (filled points), for q (slowest to fastest decay) of 0.0001 ($\otimes$) , 0.001 ($\bigcirc$), 0.003 ($\square$), 0.01 ($\triangle$), 0.02 ($\diamond$), 0.04 ($\triangle$), 0.08 ($\bigcirc$), and 0.3 ($\square$).

with a drastic change in slope being apparent near $t = 100$. The long-time relaxation of $g^{(1s)}(q,t)$ is not a simple exponential; it is seen to retain a slight curvature. Our model thus leads to non-exponential relaxations of $g^{(1s)}(q,t)$.

Figure 2b presents $g^{(1s)}(q,t)$ as a function of q^2 for various values of t. Just as $\log(g^{(1s)}(q,t))$ does not decay linearly in t, so also $\log(g^{(1s)}(q,t))$ does not decay linearly in q^2.

Finally, Figure 2c compares the measured $g^{(1s)}(q,t)$ with the Gaussian Diffusion Approximation prediction $g^{(1s)} \sim \exp(-q^2\langle(\Delta x(t))^2\rangle/2)$. At the largest q we examined, $g^{(1s)}(q,t)$ as measured agrees with the Gaussian expectation. However, at such a large q, $g^{(1s)}(q,t)$ decays into the noise at very small t. At smaller q, the Gaussian expectation fails qualitatively. For $q \leq 0.04$, the experimentally measured $g^{(1s)}(q,t)$ visibly becomes bimodal, as has also been observed experimentally[17–19]: At earlier times, $g^{(1s)}(q,t)$ agrees with the Gaussian expectation. At later times, $\exp(-q^2\langle(\Delta x(t))^2\rangle/2)$ (filled points) falls rapidly with increasing t, but the measured $g^{(1s)}(q,t)$ (open points) decreases much more slowly. As a result, in later parts of their decay $g^{(1s)}(q,t)$ and $\exp(-q^2\langle(\Delta x(t))^2\rangle/2)$ differ by orders of magnitude.

5 Discussion

The primary conclusion of this paper is that it is unjustifiable, and often incorrect, to use the Gaussian Diffusion Approximation to interpret data on the diffusion of dilute probe particles through complex fluids. In support of our conclusion we noted (Section 2) extensive experimental evidence on diffusion in polymer solutions, colloid suspensions, and glass-forming liquids. Measurements of $P(\delta x,t)$, $\langle(\Delta x(t))^2\rangle$, and $g^{(1s)}(q,t)$ all show that diffusion in these complex fluids is described by non-Gaussian processes.

The Gaussian Diffusion Approximation is sometimes invoked to claim that mean-square particle displacements can be calculated from dynamic light scattering spectra via a relation

$$g^{(1s)}(q,t) = \exp(-q^2\langle(\Delta x(t))^2\rangle)/2). \quad (19)$$

Because the Gaussian Diffusion Approximation is generally incorrect in complex fluids, Eq. 19 cannot be used to interpret the motion of particles through complex fluids. While Eq. 19 is found in standard texts on dynamic light scattering[1], it appears there in the context of experiments on dilute macromolecules in simple low-viscosity solvents, notably water, these being the experiments that were *au courant* for light scattering spectroscopy at the time that Ref. 1 was written. Fortunately, Doob's Theorem sometimes gives us an entirely reliable warning that Eq. 19 cannot possibly be valid in a system, namely if $g^{(1s)}(q,t)$ is not a simple exponential in q^2 and in t then $g^{(1s)}(q,t)$ cannot possibly be consistent with the Gaussian Diffusion Approximation. The Gaussian Diffusion Approximation is also sometimes invoked implicitly, notably in studies that report $\langle(x(t))^2\rangle$ rather than the full $P(\Delta x,t)$. However, the mean-square displacement only characterizes diffusive motions in the special case that the Gaussian Diffusion Approximation is applicable.

In principle, $P(\Delta x,t)$ should be experimentally accessible by measuring $g^{(1s)}(q,t)$ at fixed t for an adequate range of scattering vectors q, and then performing a Fourier transform from q to Δx to advance from $g^{(1s)}(q,t)$ to $P(\Delta x,t)$. Significant obstacles to such an experiment, which to the author's knowledge has not been performed, would include sweeping an adequate range of q and determining the absolute calibration of the spectral amplitude as the scattering angle or the illuminating wavelength are changed.

It appears worthwhile to note that there are generalizations of the Langevin picture, distinct from the one advanced by Tateishi[23] and seen in operation in the walking confined diffusion model[24,25], that lead only to Gaussian behavior. Mandelbrot and Van Ness[29] discuss fractional Brownian motion. Fractional Brownian motion differs from the Brownian motion generated by the Langevin equation (eq 7) in that the simple

random force $\mathscr{F}(t)$ is replaced with an integral average

$$\mathscr{F}_M(t) = \int ds\, K(s)\mathscr{F}(t-s) \qquad (20)$$

of random forces applied at different times, $K(s)$ being a memory kernel. The simple random force had a vanishingly short correlation time, so that $\langle\mathscr{F}(t)\mathscr{F}(t+s)\rangle \sim \delta(s)$, $\delta(s)$ being the Dirac delta function. In fractional Brownian motion, $K(s)$ is non-zero over an extended range of values of s, so that the random increments supplied to dx/dt by $\mathscr{F}_M(t)$ at different times are cross-correlated. Mandelbrot and Van Ness[29] specifically considered a power-law memory kernel. So long as $\mathscr{F}_M(t)$ is a sum of *identically distributed* Gaussian random variables, it is itself a Gaussian random variable, so the distribution of displacements $P(\Delta x, t)$ generated by fractional Brownian motion remains Gaussian.

Closely related to fractional Brownian motion are the motions described by the generalized Langevin equation

$$m\frac{d^2x}{dt^2} = -\int_{-\infty}^{t} ds\, \phi(t-s)\frac{dx(s)}{dt} + \mathscr{F}(t), \qquad (21)$$

as discussed by Fox[30], with memory kernel $\phi(t-s) = k_B T m^2 \langle\mathscr{F}(t)\mathscr{F}(s)\rangle$, and k_B and T being Boltzmann's constant and the absolute temperature, respectively. The random force $\mathscr{F}(t)$ is taken to be a non-Markoffian Gaussian random process, non-Markoffian because $\phi(t) \neq a\delta(t)$. As emphasized by Fox[30], $dx(t)/dt$ inherits from $\mathscr{F}(t)$ its Gaussian-random non-Markoff nature, so that $x(t)$ remains Gaussian, even though it is not a Markoff process.

The models of Mandelbrot and Ness, and of Fox, differ from Tateishi, et al.'s model in a fundamental respect. In both of these models the thermal driving force is a sum of *identically distributed* random forces, so a Gaussian $P(\Delta x, t)$ is necessarily found. In the Tateishi, et al., model, there are two simultaneous, differently-distributed random forces; rationales based on the Central Limit Theorem are therefore inapplicable, and a non-Gaussian $P(\Delta x, t)$ can be obtained.

Finally, I note several experimental techniques whose data interpretation sometimes relies on the Gaussian Diffusion Approximation.

Inelastic scattering methods, including quasielastic light scattering, quasielastic x-ray scattering, and inelastic neutron scattering, when applied to systems in which the scatterers are dilute, all measure $g^{(1s)}(q,t)$. For each of these methods, the results above are all applicable. For probes in complex fluids, eq 5 is invalid. If one used $g^{(1s)}(q,t)$ to infer the mean-square displacement, at long times and smaller q the inferred mean-square displacement would be too small, and the inferred time-dependent microviscosity would be too large.

Pulsed-Field-Gradient Nuclear Magnetic Resonance generally[31] infers a self-diffusion coefficient via the Stejskal-Tanner equation[32], which in standard derivations[31] inserts the effect of diffusion on spin relaxation via the Fick's Second Law operator $D\nabla^2$, D being a constant. The use of Fick's second law is equivalent to the Gaussian Diffusion Approximation. Use of the Stejskal-Tanner equation and PFGNMR to infer self-diffusion coefficients of objects in complex fluids therefore requires careful attention. In particular, if the relaxation identified as corresponding to self-diffusion is not a simple exponential (cf. fig 2a), then the Gaussian Diffusion Approximation and hence the Stejskal-Tanner equation would certainly not be applicable to the system.

Particle tracking techniques are sometimes only used to determine $\langle(\Delta x(t))^2\rangle$ rather than the full $P(\Delta x, t)$. If the mean-square displacement is interpreted directly as a time-dependent diffusion coefficient, the Gaussian approximation has been invoked implicitly, namely the relationship between $\langle(\Delta x(t))^2\rangle$ and Dt is part and parcel of the Gaussian approximation. Fluorescence photobleaching recovery and fluorescence correlation spectroscopy sometimes assume a form for $P(\Delta x, t)$ and after complex averaging advance to infer the time dependence of $\langle(\Delta x(t))^2\rangle$. If the assumed form is Gaussian, but $\langle(\Delta x(t))^2\rangle$ does not increase linearly in t, the analysis is not self-consistent.

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Graphical TOC Text

In a complex fluid, the displacement distribution function $P(\Delta x, t)$ is generally not a Gaussian in Δx; data interpretations using the Gaussian Diffusion Approximation are often invalid.