In complex fluids the Gaussian Diffusion Approximation is generally invalid

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Supplemental Material

Mindful that some of the computational results may not have been entirely expected, a more detailed description of the computation follows. The material here is an amplification of the material in the paper in the section Simulations; additional material has been interpolated:

A starting point for simulations is the Langevin equation

$$m\frac{du(t)}{dt} = -f_o u(t) + \mathscr{F}(t), \qquad (1)$$

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. 1 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[1,2] 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 increased linearly with t.

This section discusses an adequate minimal analytic model for a complex fluid, and our computational implementation of it. Our results are based on the Mori-Zwanzig equation[3], which is an exact rearrangement of the physically-exact Liouville equation for the time evolution of all classical systems. The Mori-Zwanzig equation[3] provides

$$m\frac{du(t)}{dt} = i\Omega u(t) - \int_{-\infty}^{t} ds\phi(s)u(t-s) + F^P(t). \qquad (2)$$

Here $u(t)$ is the dynamic variable of interest, in this work the probe velocity. For our systems Ω vanishes by time reversal symmetry. $F^P(t)$ is the Mori-Zwanzig projected force. The Mori-Zwanzig theorem gives an exact expression for $F^P(t)$ in terms of the system Hamiltonian. The Mori memory kernel is

$$\phi(s) = \langle F^P(0)F^P(s)\rangle / \langle (u(0))^2\rangle. \qquad (3)$$

The Mori-Zwanzig equation looks a great deal like the Langevin equation. However, the Langevin equation is a heuristic approximant. The Mori-Zwanzig equation is an exact result of classical and statistical mechanics. In particular, Mori-Zwanzig theorem gives an exact – albeit difficult to evaluate – formula for the memory kernel $\phi(s)$.

Equations 1 and 2 are fundamentally different. Eq 1 is often interpreted as a stochastic differential equation. Eq 2 is a conventional differential equation: It is Newton's second law of motion, rewritten by partitioning the forces between Ω, $\phi(s)$, and $F^P(t)$. $F^P(t)$ is determined by the positions and motions of the other particles in the system, so it is continuous, differentiable, and integrable. Features associated with integrating stochastic differential equations[4] do not arise with the Mori-Zwanzig equation.

$F^P(t)$ is often approximated as having a correlation time short compared to the time scales of interest. With this approximation, $F^P(t)$ is approximated by a Markoff process, while $\phi(s)$ is approximated as being very nearly $\sim \delta(s)$, so that the Mori-Zwanzig equation is approximated by the Langevin equation. For a complex fluid, these approximations are lose all the interesting behavior. In interesting complex fluids, relaxations occur on multiple observable time scales. Probe motions are observed on the time scales on which relaxations occur. On these time scales, $F^P(t)$ is not even approximately a Markoff process; it instead has prolonged correlations related to the prolonged correlations in the surrounding fluid.

As noted in the discussion, it is inadequate to model $F^P(t)$ as a single random process having long-lived correlations. Models of this sort lead to Gaussian forms for $P(\Delta x,t)$ and are thus inconsistent with experiment. A correct solution was developed by Tateishi, et al.[5]. Just as a probe diffusing in a polymer solution experiences uncorrelated interactions with solvent and polymer molecules, so also does Tateishi's gen-

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eralized Langevin equation contain 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. Because $\xi(t)$ and $\eta(t)$ were taken to be uncorrelated, the corresponding memory kernel was

$$\phi(\tau) = \langle \xi(t)\xi(t+\tau)\rangle + \langle \eta(t)\eta(t+\tau)\rangle. \quad (4)$$

$\xi(t)$ and $\eta(t)$ have different distributions, so their sum is not a sum of identically distributed random variables; the Central Limit Theorem and Doob's Theorem do not apply to their sum. Tateishi's analytic calculation of $\langle(\Delta x(t))^2\rangle$, based on this model, found distinct diffusive and subdiffusive regimes.

Our molecular-dynamics computer calculations differ from Tateishi, et al.'s in that we used an exponential memory, we calculated $P(\Delta x,t)$ itself, and furthermore calculated multiple statistical characterizations and transforms of $P(\Delta x,t)$. The principal challenge in our calculations was in generating an $F^P(t)$ with well-defined correlations, together with a mutually consistent $\phi(t)$. This problem was in principal solved by Mori with his orthogonal hierarchy of thermal forces scheme[6]. The basis of the hierarchy is Mori's observation that the Mori-Zwanzig equation is valid for an arbitrary dynamic mechanical variable, the thermal force $F^P(t)$ is itself a dynamic mechanical variable, so therefore the time evolution of $F^P(t)$ can be calculated with a new Mori equation. The new Mori equation generates the time evolution of $F^P(t)$ in terms of a second Mori memory kernel and a second thermal force. Each thermal force $F^P(t)$ can in turn be written as being generated by a higher-order memory kernel and thermal force. The orthogonal hierarchy automatically leads to a mutual consistency between each ϕ and the corresponding $F^P(t)$.

Here we used Mori's orthogonal hierarchy purely as a mathematical device to generate the needed $F^P(t)$ and consistent $\phi(t)$. Our approach is to truncate the hierarchy at some order, and use the highest-order equation as a generalized Langevin equation that generates projected forces and corresponding memory functions having the desired temporal calculations.

In the following calculations a complex fluid is modelled as supplying two independent projected forces. One is a rapidly-fluctuating solvent force corresponding to the simple hydrodynamic drag $-f_o v$ on the probe. The other is a slowly-fluctuating projected force corresponding to polymer matrix motions. Because these are physical forces, their time integrals are well-behaved. The presence of two distinct projected forces is critical to obtaining our results.

Simulations were run on an 448 core Nvidia Tesla C2075 processor (nominal maximum single-precision speed, 1.15 teraflops) using the Portland Group PGFortran optimizing compiler for Fortran 90. Individual simulations ran for $\sim 5\cdot 10^9$ particle displacement steps. The direct outcomes of each simulation were a velocity trajectory u_i and a position trajectory x_i, i being the discrete time variable. u_i^2 was confirmed to have no secular drift over the course of a simulation, confirming that the system remained in thermal equilibrium.

Throughout the simulations, changes in the position were computed from the u_i as

$$x_i = x_{i-1} + u_i \Delta t. \quad (5)$$

Notional units such that $\Delta t = 1$ were used throughout.

The final software test was a simulation of the Langevin equation. The Langevin equation for the velocity was used in its discrete-time form for a unit-mass particle

$$u_i = u_{i-1} - f_o u_{i-1}\Delta t + X_i \Delta t \quad (6)$$

Here i labels the time steps. X_i is a net impulse, the integral of the projected force over the time interval between moments $i-1$ and i. In the Langevin simulation, X_i and X_j for $i \neq j$ were independently generated Gaussian random variables.

For the complex fluid simulation, we added to the Langevin equation a second projected force, a projected force having an extended correlation time, and its corresponding memory function. The long-lived projected force was constructed as a sum over Markoff sources Y_j, the effect of these sources being propagated forward from time j to time i by propagators C_{i-j}, namely

$$F_i^P = \sum_{j=0}^{i} Y_j C_{i-j} \quad (7)$$

The propagators C_{i-j} have a range N, meaning that they are only non-zero for $\mid i-j \mid < N$. During the course of a simulation $i \gg N$. The F_i^P are constructed as sums of Gaussian random processes, so the probability distribution of F_i^P must also be a Gaussian random process, as was confirmed in the simulations. However, C_{i-j} is non-zero for $i-j \neq 0$, so the long-lived F_i^P are cross-correlated; the long-lived F_i^P do not follow a Markoff process.

From eq 3, the Mori kernel for the second projected force may be written in terms of the propagator as

$$M_{b-a} \equiv \langle F_a^P F_b^P\rangle = \left\langle \sum_{i=1}^{a}\sum_{j=1}^{b} Y_i C_{a-i} Y_j C_{b-j} \right\rangle, \quad (8)$$

with $a \gg N$ and $b \gg N$. For $b-a \geq 0$ and

$$\langle Y_i Y_j\rangle = m_1^2 \delta_{i-j}, \quad (9)$$

with δ_{i-j} being the Kronecker delta, M_{b-a} simplifies to

$$M_j = m_1^2 \sum_{i=0}^{N} C_i C_{i+j}. \quad (10)$$

Our propagator was an exponential

$$C_i = f_1 \exp(-ai)/Q \quad (11)$$

with f_1 being the strength of the propagator, the normalizing factor Q being arranged so that

$$f_1 = \sum_{i=0}^{N} C_i. \tag{12}$$

By direct calculation, for an exponential propagator the memory kernel is also an exponential, namely

$$M_j = \left[f_1^2 \sum_{i=0}^{N} \exp(-2ai)/Q^2 \right] \exp(-aj) \tag{13}$$

the quantity in brackets being a constant independent of j.

We also tested propagators that initially followed eq 11, but at times $i > a^{-1}$ followed a power law

$$C_i = f_2 (ia)^{\nu}/(Qe), \tag{14}$$

with f_2 chosen so that C_i was continuous at the crossover point.

The discrete-time Mori equation finally becomes

$$u_i = (u_{i-1} + X_i + \sum_{j=0}^{N} (C_j Y_{i-j} - M_j u_{i-j}))(1 - f_o). \tag{15}$$

The u_i are driven by two different statistical processes, one having an extended memory, so neither the Central Limit Theorem (which requires for the random force a sum of *identical* processes) nor Doob's Theorem (which refers to Markoff processes) is applicable to the behavior of the u_i.

Having generated the statistical processes u_i and x_i for 5 billion steps (plus initial thermalization), characterizations of these processes followed. For ease of reading, the characterizations are written with time as the continuous variable t. For each system we calculated the displacement distribution function $P(\Delta x, t)$, the velocity-velocity correlation function

$$C_{VV}(t) = \langle u(0) u(t) \rangle, \tag{16}$$

and the acceleration-acceleration correlation function

$$C_{AA}(t) = \langle (u(t_2) - u(t_1))(u(t_4) - u(t_3)) \rangle. \tag{17}$$

Here $\Delta x(t) = x(\tau + t) - x(\tau)$. The function $C_{AA}(t)$ was evaluated for $t_1 \le t_2 \le t_3 \le t_4$, with $t = t_3 - t_2$, while keeping $t_2 - t_1$ and $t_4 - t_3$ small. $P(\Delta x, 1)$ gives the distribution of $x_i - x_{i-1}$, which is the same as the distribution of the u_i. The u_i had the expected Gaussian distribution.

The velocity-velocity correlation functions are long lived, so errors in eq 5 due to time being discretized were small. For the simple Langevin model, the velocity-velocity correlation function was accurately exponential, demonstrating that $f_o \Delta t$ was not too large. The time-dependent mean-square displacement

$$K_2(t) = \langle (\Delta x(t))^2 \rangle \tag{18}$$

was computed directly, not from $P(\Delta x, t)$. Plots of $P(\Delta x, t)$ were generated at each t by binning values of $P(\Delta x, t)$ using $0.1\sqrt{(K_2(t))}$ as the bin width.

Unless $P(\Delta x, t)$ is a Gaussian, characterizing $P(\Delta x, t)$ requires all even central moments K_{2n} of Δx. We calculated the time-dependent K_4 and K_6 from the simple moments $\langle (\Delta x(t))^n \rangle$ as

$$K_4 = (\langle (\Delta x(t))^4 \rangle - 3(\langle (\Delta x(t))^2 \rangle)^2)/(\langle (\Delta x(t))^2 \rangle)^2 \tag{19}$$

and

$$K_6 = (\langle (\Delta x(t))^6 \rangle - 15 \langle (\Delta x(t))^4 \rangle \langle (\Delta x(t))^2 \rangle + 30 \langle (\Delta x(t))^2 \rangle^3)/(\langle (\Delta x(t))^2 \rangle)^3. \tag{20}$$

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.

The intermediate scattering function

$$g^{(1s)}(q,t) = \langle \cos(q \Delta x(t)) \rangle \tag{21}$$

was determined for a wide range 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. Such precision is not always found in experimental studies. In the subfield of microrheology, it is sometimes presumed that $g^{(1s)}(q,t)$ is related to the mean-square displacement via

$$g^{(1s)}(q,t) = \exp(-q^2 \langle (\Delta x(t))^2 \rangle / 2), \tag{22}$$

as is the case for particles described by the Langevin equation. This hypothesis was tested by plotting the directly-calculated (eq 21) and inferred (eq 22) values for $g^{(1s)}(q,t)$ against each other for various q and t.

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