Stochastic Dynamics in Irreversible Nonequilibrium Environments. 1. The Fluctuation−Dissipation Relation

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A generalization of the generalized Langevin equation (stochastic dynamics) is introduced in order to model chemical reactions which take place in changing environments. The friction kernel representing the solvent response is given a non-stationary form with respect to which the instantaneous random solvent force satisfies a natural generalization of the fluctuation−dissipation relation. Theoretical considerations, as well as numerical simulations, show that the dynamics of this construction satisfy the equipartition theorem beyond its equilibrium limits.

I. Introduction

Much of the work performed to date on chemical reactions (or, more generally, dynamics) in fluids has concentrated on those reactions which have a single easily identifiable reaction coordinate coupled to the fluid through a uniform fluid response.[1−6] The Langevin models proposed by Kramers,[1] and their extensions, are the paradigmatic examples of this approach, and much progress has been made in their study.[7−14] The primary extensions of the Langevin equation use colored noise[7,15] and/or space-dependent friction[16−20] and are often called generalized Langevin equations (GLEs).[11] In the present work, we will further generalize to the case where the friction is nonstationary, i.e., explicitly dependent on the absolute time. This irreversibility (nonstationary behavior) is assumed to be a manifestation of a bath which is driven to a different macrostate either by an external force or perhaps a collective internal phenomenon. Note that the term "irreversibility" is not being used here to describe the nonequilibrium behavior of the chosen coordinate in an otherwise equilibrium environment—the usual case of a stationary, albeit colored, GLE. Rather, an irreversible GLE (iGLE) is defined here as one in which the *environment* is not in a stationary equilibrium, leading to a time-dependent change in how the environment responds to the chosen coordinate.

There are several physical problems in which the generality of the iGLE beyond that of GLE's is necessary to describe the dynamics. For example, consider a bath which is undergoing a smooth isothermal contraction. Such a change would lead to increased solvent friction, and would change the dynamics of the chosen (reaction) coordinate to which it is coupled. A more complex class of problems arises if the friction in the iGLE represents events which are occurring throughout the fluid, and consequently the properties of the fluid (i.e., the environment or the solvent bath) change as a result of the motion of the chosen coordinate. An application of this reaction-induced, viz. chemistry-induced, irreversibility in the solvent will be pursued in paper 2 of this series.[21] It models polymerization in the thermosetting regime in which the fluid undergoes a rather dramatic chemistry-induced phase transition from liquid to glass/melt.

The aim of the present paper is to construct a general class of valid iGLEs. In the present work, however, we will assume that there is a constant and fixed temperature. The generality to nonfixed temperatures encompasses the important problem of temperature-ramped chemical kinetics and is reserved for a future study. Fixed-temperature GLEs satisfy the fluctuation−dissipation theorem if and only if they satisfy the equipartition theorem.[22] Similarly, the iGLEs will be required to satisfy the equipartition of energy in various limits for a broad class of irreversible changes in the solvent environment. In section II, a form of the iGLE will be constructed which is appealing in that the construction requires the correlation function of the random forces to satisfy a natural nonstationary extension of the fluctuation−dissipation relation. In section III, it will be shown that such a requirement is necessary for the dynamics of the iGLE to have a velocity autocorrelation function which satisfies the equipartition theorem in equilibrium and quasi-equilibrium limits. Finally, in section IV, a simple model of an irreversible environment will illustrate the claimed behavior. Each parametrization of this model involves a change in the friction constant (due to the solvent) from a lower friction to a higher friction regime, illustrating the isothermal compression discussed above.

II. Generalization of the GLE

The generalized Langevin equation (GLE)[6,23] can be written as

$$\dot{v} = -\int^{t} dt'\, \gamma(t,t')v(t') + \xi(t) + F(t) \tag{1}$$

where $F(t)$ ($\equiv -\nabla_q V(q(t))$) is the external force, v ($=\dot{q}$) is the velocity, q is the mass-weighted position, $\xi(t)$ is the random force due to a solvent, and $\gamma(t,t')$ represents the response of the solvent from the past to the present. The latter quantity is usually written as a stationary friction kernel $\gamma_0(t-t')$—a function only of the time difference $t-t'$. (In the well-known Ohmic limit, in which γ_0 is proportional to a delta function, eq 1 reduces to the ordinary Langevin equation.) Assuming that the solvent is thermalized, the second fluctuation-dissipation (FD) theorem[22] relates the random force and the friction kernel, i.e.,

$$\langle \xi(t)\xi(t') \rangle = k_B T \gamma_0(t-t') \tag{2}$$

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where k_B is Boltzmann's constant and T is the temperature. Recall that, for an arbitrary function $f(t)$ in time, the Fourier and Fourier−Laplace transforms in frequency space ω may be written as

$$f(\omega) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-i\omega t} f(t) \tag{3a}$$

$$f[\omega] \equiv \int_{0}^{\infty} \mathrm{d}t\, \mathrm{e}^{-i\omega t} f(t) \tag{3b}$$

respectively. The FD relation in eq 2 may thus be written in frequency space as

$$\langle \xi(\omega)\xi^*(\omega')\rangle = \frac{k_B T}{\pi}\gamma_0[\omega]\delta(\omega - \omega') \tag{4}$$

This form will be of use in subsequent sections.

In the present work, we generalize the GLE to include a nonstationary component in the solvent. Since the solvent will presumably also come to equilibrium at long-enough time, we impose the requirement that the friction kernel must become stationary at long time. In symbols this means that for absolute times $t,t' \to \infty$,

$$\gamma(t,t') \to g_\infty^2 \gamma_0(t-t') \tag{5}$$

where g_∞ is a constant and γ_0 is stationary. If the random force in eq 1 is also set at $t \to \infty$ according to

$$\xi(t) \to g_\infty \xi_0(t) \tag{6}$$

where ξ_0 satisfies relation 2 with respect to γ_0, then the FD theorem is ipso facto satisfied at long time. This leads to a well-defined temperature T, which is related to the equipartition of the kinetic energy at long time. It should be noted that the requirements in eqs 5 and 6 are stronger than what is strictly necessary to ensure equilibrium in the infinite future. The given expressions simply provide for a change in the static friction between the infinite past and the infinite future. However, a weaker requirement would also permit a different relaxation time in the stationary limit, i.e., the stationary friction in eq 5 would be different than γ_0. This weaker requirement, which provides a wider range of dynamics, will be pursued in future work.

From the arguments above, one can write

$$\gamma(t,t') \equiv \gamma_1(t,t')\gamma_0(t-t') \tag{7}$$

where the equation serves to define γ_1. The associated random force can also be written as

$$\xi(t) \equiv g_1(t)\xi_0(t) \tag{8}$$

where ξ_0 satisfies the FD relation with respect to γ_0 and the expression serves to define $g_1(t)$. In order to satisfy the long-time condition, we have the following constraints:

$$\lim_{t\gg 0} \gamma_1(t,t') = g_\infty^2 \tag{9a}$$

$$\lim_{t\gg 0} g_1(t) = g_\infty \tag{9b}$$

To complete the statement of the problem, a condition relating $\gamma_1(t,t')$ and $g_1(t)$ is needed.

The simplest form for $\gamma_1(t,t')$ which is symmetric and separable in the two times is

$$\gamma_1(t,t') = g(t)g(t') \tag{10}$$

where $g(t)$ serves to define the irreversible change in the environment. (As will be illustrated in section (IV), this form is sufficient to provide a large variety of dynamics not seen with the usual GLEs.) The stochastic equations of motion for an iGLE may thus be written as

$$\dot{v}(t) = -\int^{t} \mathrm{d}t'\, g(t)g(t')\gamma_0(t-t')v(t') + g_1(t)\xi_0(t) + F(t) \tag{11}$$

where g and g_1 characterize the nonequilibrium behavior, and γ_0 is a stationary friction kernel related to the (stationary) random force $\xi_0(t)$ through the FD relation.

According to eqs 9, $g(t)$ and $g_1(t)$ are equal at long time, taking the same value g_∞. The following heuristic argument suggests that they should be set equal for all time: Physically, g_1 modulates the instantaneous fluctuations in the environment while g modulates the instantaneous response by the environment. Hence, whenever the subsystem and the solvent form a quasi-equilibrium, these quantities must be equal according to the FD theorem. The strong requirement that $g = g_1$ for all time simply ensures that no violations are permitted. It is thus sufficient. Is it necessary? Yes, because otherwise one would have to anticipate the quasi-equilibria that would be induced by g and g_1 in determining these functions a priori. It should also be noted that if $g = g_1$, then by construction,

$$\begin{aligned}\langle \xi(t)\xi(t')\rangle &= k_B T g(t)g(t')\gamma_0(t-t') \\ &= k_B T\gamma(t,t')\end{aligned} \tag{12}$$

which is appealing as a natural extension of the FD relation to a nonstationary friction kernel. It has been argued that $g(t)$ and $g_1(t)$ should be set equal to each other, and in the next section we will show that this requirement is tantamount to requiring equipartition of energy in local-equilibrium environments.

The fact that the system defined through eq 11 obeys the generalized FD relation in eq 12 is clearly a consequence of the separability of the nonstationary friction kernel in eq 10. The latter is a strong requirement on the behavior of the random force in so far as it requires that all bath modes be affected equally. Nonetheless, the class of systems that are defined by the iGLE of eq 11 do exhibit the types of dynamical behavior that nonstationary GLE's provide, and are therefore interesting in their own right. Further work exploring the construction of these nonstationary iGLEs from mechanical systems using the projection operator formalism[2] is also in progress.

III. Local Harmonic Analysis

After a little algebra, harmonic analysis of eq 11 (assuming that there is no external Force, i.e., $F(t) = 0$) leads to the following integral expression in frequency space:

$$\begin{aligned} i\omega v(\omega) = -\int_{-\infty}^{\infty} \mathrm{d}\omega_1 \int_{-\infty}^{\infty} \mathrm{d}\omega_2\, g(\omega - \omega_1)\gamma_0[\omega_1] \times \\ g(\omega_1 - \omega_2)v(\omega_2) + \int_{-\infty}^{\infty} \mathrm{d}\omega_1\, g_1(\omega - \omega_1)\xi_0(\omega_1) \end{aligned} \tag{13}$$

which, because of the irreversibility, is not of a simple algebraic form. Note that ignoring $F(t)$ in this analysis does not result in loss of generality because a nonzero $F(t)$ would be uncorrelated with the random fluctuations and hence would not affect them. In the next subsection, this expression will be shown to reduce to the usual result in the stationary limit. In the subsequent subsection, a similar expression will be derived for quasi-equilibrium regimes, showing that equipartition of energy is satisfied during such regimes if the equality $g(t) = g_1(t)$ holds. This is the result which was anticipated in the heuristic argument at the end of section II, providing us with the claim that the equality should hold for all time.

A. Stationary Limit. In the stationary limit, $g(t)$ and $g_1(t)$ must be constant for all time, and as a consequence their Fourier transforms may be written as

$$g(\omega) = g\delta(\omega) \tag{14}$$

$$g_1(\omega) = g_1\delta(\omega) \tag{15}$$

Substitution into eq 13 leads to the result

$$v(\omega) = \frac{g_1\xi_0(\omega)}{i\omega + g_2\gamma_0[\omega]} \tag{16}$$

Recall that the power spectrum of a random stationary process $f(t)$ is given by

$$I_f(\omega) = \langle f(\omega)f^*(\omega)\rangle \tag{17}$$

in terms of its Fourier transform $f(\omega)$. The corresponding power spectra of the processes, v and ξ_0, are therefore related by

$$I_v(\omega) = \frac{{g_1}^2 I_{\xi0}(\omega)}{|i\omega + g^2\gamma_0[\omega]|^2} \tag{18}$$

$$= \left(\frac{k_B T}{\pi}\right)\frac{{g_1}^2 R\ \{\gamma_0[\omega]\}}{|i\omega + g^2\gamma_0[\omega]|^2} \tag{19}$$

where the second equality is obtained through the use of eq 4. The correlation function in time t is readily obtained by an inverse Fourier transform of eq 19,

$$\langle v(t_0)v(t_0 + t)\rangle = \left(\frac{k_B T}{2\pi}\right)\int_{-\infty-i\epsilon}^{\infty-i\epsilon} d\omega \frac{g_1^2 e^{i\omega t}}{i\omega + g^2\gamma_0[\omega]} \tag{20}$$

In the $t = 0$ limit, the integral can be obtained by Cauchy's residue theorem giving

$$\langle v^2\rangle = \left(\frac{g_1^2}{g^2}\right)k_B T \tag{21}$$

which gives the equipartition result equal to twice the kinetic energy if $g_1 = g$. This calculation can be found in Kubo et al.[24] for example, in the well-known case that $g = g_1 = 1$, leading to the equipartition of energy for colored friction. We thus conclude that the equipartition result is satisfied if and only if $g = g_1$, not necessarily unity.

The result that $g = g_1$ in the stationary case could also have been shown immediately through the following simple syllogism: The equality is satisfied for long time; the two values are constant as a function of time; therefore the equality is satisfied for all time. The point of showing the detailed derivation leading to eq 19 is that (*i*) it explicitly shows that the long-time limit of the iGLE, as defined, must satisfy the equality between g and g_1 (and correspondingly the FD relation), as claimed earlier, and (*ii*) the derivation plays a role in the quasi-equilibrium limits of the nonstationary case to be discussed in the next subsection.

B. Quasi-Equilibrium. We now consider eq 11 in nonstationary regimes in order to prove that the equality between g and g_1 is necessary, in general. If $\gamma_0(t)$ decays quickly, and the driving force $g_1(t)$ on the environment changes relatively slowly, then we obtain an instantaneous version of the FD relation, satisfied adiabatically, only if the aforementioned equality holds. To make this statement precise, we define a *quasi-equilibrium state* at time $\bar{t}$ as a state in which there exists a time difference, δ, such that the stationary friction kernel $\gamma_0(t)$ is essentially zero outside of the interval $I_{\bar{t}}$ ($\equiv(\bar{t} - \delta, \bar{t} + \delta)$), and the external driving functions $g(t)$ and $g_1(t)$ are essentially constant on this interval. (The only indeterminacy in this definition lies in the meaning of "essentially," which practically can be taken to mean that the errors are small; a more careful analysis using controlled error estimates yields the same result.)

Under the quasi-equilibrium condition, eq 11 reduces to

$$\dot{v}(t) = -g(\bar{t})^2\int^t dt'\gamma_0(t-t')v(t') + g_1(\bar{t})\xi_0(t) + F(t) \tag{22}$$

for t in the interval $I_{\bar{t}}$. We now consider a "local harmonic analysis" of this equation in which we limit the Fourier transform of eq 3a to the interval $I_{\bar{t}}$, i.e., for some arbitrary function $f(t)$, let

$$\tilde{f}(\omega) \equiv \frac{1}{2\pi}\int_{\bar{t}-\delta}^{\bar{t}+\delta} dt\ e^{-i\omega t} f(t) \tag{23}$$

which reverts to the Fourier transform in the limit that δ goes to infinity. The result of such an analysis is

$$i\omega\tilde{v}(\omega) = -g(\bar{t})^2\gamma_0[\omega]\tilde{v}(\omega) + g_1(\bar{t})\tilde{\xi}_0(\omega) \tag{24}$$

The surface terms vanish because, by assumption, δ is "long" compared to the decay time in γ_0, leading to a zero contribution to the short frequency components. The Fourier transformed stationary kernel $\gamma_0[\omega]$ is not restricted to the interval $I_{\bar{t}}$ because of the requirement that $\gamma_0(t)$ have negligible contribution for $t > \delta$. The quantities $\tilde{v}$ and $\tilde{\xi}_0$ are implicitly dependent on $\bar{t}$ and δ through their dependence on the region of integration $I_{\bar{t}}$.

The quasi-equilibrium equation of motion in frequency space, eq 24, is of the same structure as the equilibrium expression, eq 16. Following a similar analysis as above, we can conclude that the equipartition theorem is satisfied in quasi-equilibria only if

$$g(\bar{t}) = g_1(\bar{t}) \tag{25}$$

at characteristic times $\bar{t}$ of said quasi-equilibria. If $g_1(t)$ moves slowly (adiabatically) from quasi-equilibrium to quasi-equilibrium, then $g(t) = g_1(t)$ and, in fact, there is little effect on the dynamics due to the fact that the nonstationary friction kernel depends on *both* $g(t)$ and $g(t')$. In nonadiabatic regimes, the two-time dependence of $\gamma(t,t')$ does come into play, and the adiabatic approximation breaks down. Nonetheless, the system may find itself in quasi-equilibrium regimes long before the solvent [through $g_1(t)$] is allowed to go to equilibrium. In these cases, the fact that such quasi-equilibria are possible, (and that equipartition during them is satisfied only if the equality $g(t) = g_1(t)$ holds, leads us to the claim that the equality must be satisfied for all time. Thus, as a consequence of requiring equipartition during quasi-equilibrium, the iGLE of eq 11 must satisfy the nonstationary generalization of the FD theorem in eq 12.

IV. Results and Discussion

As in the earlier sections in which the position-dependent driving force $F(x(t))$ was set to zero, in this section, we will study several examples of the irreversible nature of the solvent [using different forms of the nonstationary friction kernel $\gamma(t,t')$] with F again set to zero.

A. Integrating the IGLE. The friction kernel in the iGLE of eq 11 takes the form (refer to eq 12)

$$\gamma(t,t') = g(t)g(t')\gamma_0(t-t') \tag{26}$$

where γ_0 is a stationary friction kernel. In the present calculations as well as those in paper 2,[21] the stationary kernel is chosen to be of the the following simple exponential form:

$$\gamma_0(t-t') = \gamma_0(0)\mathrm{e}^{-|t-t'|/\tau} \tag{27}$$

which is a good approximation to the Zwanzig−Bixon hydrodynamic friction kernel[25,26] and has been used, for example, in the landmark calculations of Straub et al.[27,28]

The FD theorem [eq 2] requires that the autocorrelation function of ξ_0 be given by

$$\langle \xi_0(t)\xi_0(t')\rangle = k_\mathrm{B}T\gamma_0(0)\mathrm{e}^{-|t-t'|/\tau} \tag{28}$$

Recall that a random variable $\xi_0(t)$ satisfying the autocorrelation function,

$$\langle \xi_0(t)\xi_0(t')\rangle = \frac{\gamma_\mathrm{G}\tau}{2}\mathrm{e}^{-|t-t'|/\tau} \tag{29}$$

can be constructed using the auxiliary Langevin equation,

$$\dot{\xi}_0(t) = -\frac{1}{\tau}\xi_0(t) + \xi_\mathrm{G}(t) \tag{30a}$$

where ξ_G is a Gaussian-distributed uncorrelated force, i.e.,

$$\langle \xi_\mathrm{G}(t)\xi_\mathrm{G}(t')\rangle = \gamma_\mathrm{G}\delta(t-t') \tag{30b}$$

Therefore, the stationary part of the random force ξ_0 can be generated by the auxiliary dynamics of eq 30 with the condition

$$\gamma_\mathrm{G} = 2\gamma_0(0)k_\mathrm{B}T/\tau \tag{31}$$

as is well known. (See, for example, ref 29.)

A minor nuance arises in the numerical integration of eq 30, due to the discrete nature of $\xi_0(t)$: If one simply integrates the equation “as is,” the variance of the resulting distribution of random forces depends on the choice of time step. A solution to this problem is given by Ermak and co-workers[30,31] and requires that we make the following correction:

$$\gamma_\mathrm{G} = \gamma_0(0)k_\mathrm{B}T\,(1 - \mathrm{e}^{-2\Delta t_\xi/\,\tau}) \tag{32}$$

where Δt_ξ is the time step in the Verlet integration of eq 30. Since the resulting behavior of ξ is continuous, the special care taken in integrating eq 30 is not necessary for the integration of the iGLE, eq 11. The usual Verlet integration of the latter can thus be carried out using a time step Δt which is an integer multiple of Δt_ξ. (Though in principle Δt_ξ can be taken to be equal to Δt, in practice, better accuracy, as exhibited by

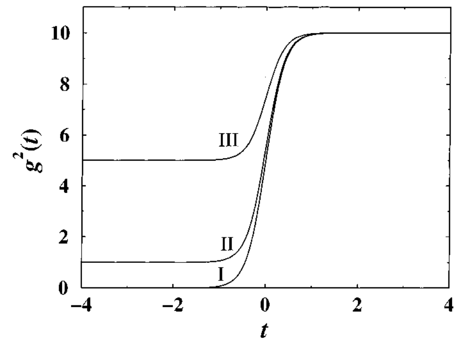

Figure 1. The square of the irreversible change in the environment $g^2(t)$ is shown here as a function of time for the three cases studied in this work.

numerical agreement with eq 29, is obtained if the stochastic equations are integrated with a multiple-timestep Verlet algorithm with $\Delta t_\xi > \Delta t$.) Newer methods[32−34] for integrating GLE’s with arbitrary stationary friction kernels were not used in these studies because in the nonstationary case they would require integral transforms of the friction kernel $\gamma(t,t')$, exchanging $(t-t')$ and ω in the Fourier cases, for example, at each time t, and this would be numerically prohibitive. A generalization of these methods to the nonstationary case of the iGLE that obviates this numerical nuisance would be of interest, and is currently being pursued.

B. Model iGLEs. In order to explore the behavior of our iGLE, all that remains is to specify the nonstationary component $g(t)$. A particularly simple choice is a "switching" function, such as

$$g^2(t) = g^2(-\infty) + \frac{1}{2}[g^2(\infty) - g^2(-\infty)]\left(1 + \frac{\mathrm{e}^{t/\tau_g} - 1}{\mathrm{e}^{t/\tau_g} + 1}\right) \tag{33}$$

which is essentially equal to the boundary values $g^2(-\infty)$ and $g^2(\infty)$ for long absolute times, $t \ll -\tau_g$ and $t \gg \tau_g$, respectively.[35] Physically, this might serve to model, for example, the increase in the system’s internal friction while undergoing an isothermal compression. Using this generic choice of $g(t)$, we performed three different sets of simulations, all sharing the following parameters: $N = 10\,000$, $k_\mathrm{B}T = 2.0$, $\gamma_0(0) = 10.0$, $\tau = 0.5$, $\tau_g = 0.2$, $\Delta t = 4.0 \times 10^{-3}$, and $\Delta t_\xi = 4.0 \times 10^{-4}$, all in arbitrary units. With the chosen values of τ and Δt, it is necessary to remember the previous 1000 friction points for each of the N trajectories. Each system was allowed to thermalize, starting at $t = -12.0$, with measurements being taken in the window $t = (-4, 4)$.[35]

The three cases to be studied all involve a switch from a low friction value in the infinite past to a high friction value in the infinite future as illustrated in Figure 1. In case I, the boundary values are taken to be $g^2(-\infty) = 0$ and $g^2(\infty) = 10.0$, representing the compression of an ideal gas (zero friction) to a fluid with large internal friction. In case II, the boundary values are taken to be $g^2(-\infty) = 1.0$ and $g^2(\infty) = 10.0$, representing the compression of a system with moderate internal friction (perhaps a dense gas). In case III, the boundary values are taken to be $g^2(-\infty) = 5.0$ and $g^2(\infty) = 10.0$, representing the further compression of an already dense liquid.

The dramatic change in the magnitudes of the friction kernel in case I can be seen in Figure 2. At $t = -4.0$ the friction kernel is very small (with the system behaving essentially as an ideal gas), but it is not precisely zero because the switching function turns on smoothly. Moreover, the response time, vis-a-vis the inverse of the slope of $\ln[\gamma(t,t')]$, at $t = -4$ is not equal to that

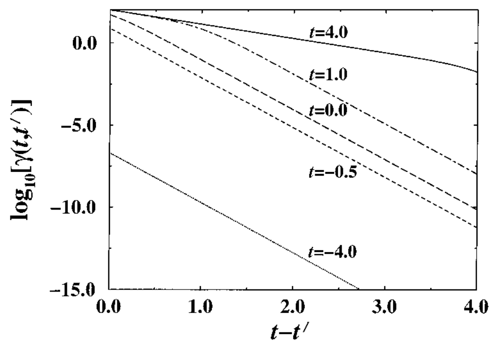

Figure 2. The logarithm of the nonstationary friction kernel $\gamma(t, t')$ in Case I is displayed at several different times t as a function of the previous times $t-t'$.

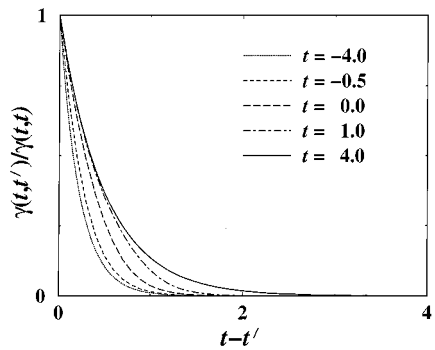

Figure 3. The nonstationary friction kernel $\gamma(t, t')$ in Case I is displayed at several different times t as a function of the previous times $t-t'$. In all cases, the abscissa is displayed as a ratio normalized to the corresponding value of $\gamma(t, t)$ so as to easily display them in one figure and better illustrate the shape of the response functions as a function of absolute time, and the time t to which each line corresponds is indicated in the legend. For the five times indicated from $t = -4$ to $t = 4$, the zero-time friction kernel $\gamma(t, t)$ takes on the values 0.21×10^{-6}, 7.6, 50, 99, and 100, respectively, as could be read off of Figure 2.

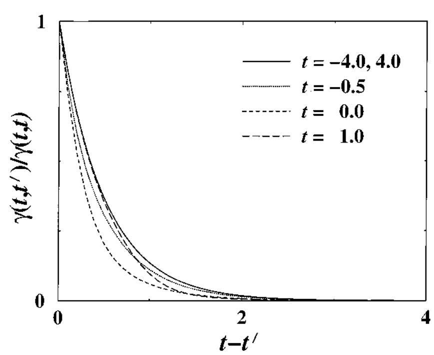

Figure 4. The nonstationary friction kernel $\gamma(t, t')$ in case II is displayed at several different times t as a function of the previous times $t-t'$. The infinite-time limits are reached at t equal -4 and 4, and both overlap as the solid line. Otherwise the curves are as in Figure 3 with the legend labeling the time t corresponding to each curve. For the five times indicated from $t = -4$ to $t = 4$, the zero-time friction kernel $\gamma(t, t)$ takes on the values 10, 16, 55, 99, and 100, respectively.

of γ_0 because it also includes the effective response due to the switching function. The latter plays a small role in cases II and III, in which the $t = -4$ behavior is dominated by the response of γ_0.

To better illustrate the $(t-t')$ dependence in the nonstationary friction kernels at different times t, the friction kernels are normalized to their equal-time value, $\gamma(t, t)$, in Figures 3 and 4 for cases I and II, respectively. (The values of $\gamma(t, t)$ for the corresponding times t are listed in the figure captions, and are

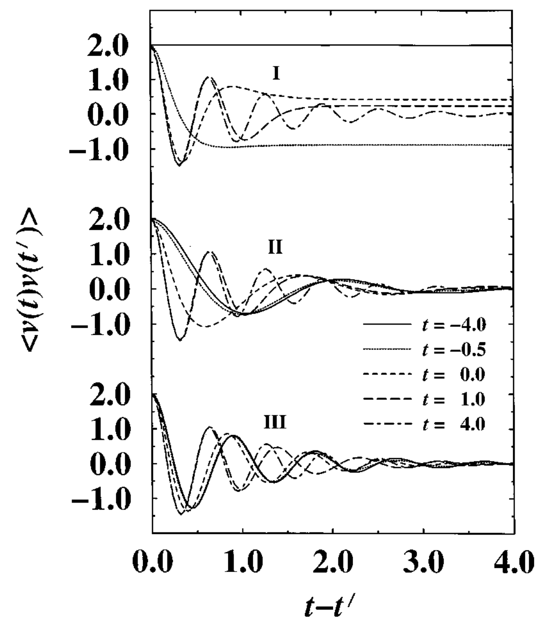

Figure 5. The autocorrelation function of the velocity, $\langle v(t)v(t')\rangle$, is displayed for each of the three cases at various initial times t as a function of the previous times $t-t'$. The curves are labeled by the corresponding time in the legend. The curves in the top, middle, and bottom segments correspond to cases I, II, and III respectively.

also illustrated explicitly for case I in Figure 2.) The shape of the normalized kernels for case III are qualitatively similar to case II, but the differences away from γ_0 are less dramatic and hence not shown. In case I, the normalized kernel is nearly zero at early times, when the motion is essentially ballistic. As the coupling to the solvent grows in, one sees that the normalized kernel both increases at the $t-t'$ origin (according to the values listed in the caption or as illustrated in Figure 2) and generally goes toward the form of the long-time normalized kernel. In this case, the small $t-t'$ values of $\gamma(t, t')$ move toward the shape of the stationary friction kernel as the system approaches the long-time equilibrium friction kernel with the oldest memory being in the least agreement. In case II, the normalized kernel at early times is essentially equal to that of the lower friction regime up to the static friction prefactor g, and hence the normalized form is equal to the $t = 4$ long time limit. At $t = -0.5$, the normalized kernel differs with the stationary kernel most strongly at the small $t-t'$ values, whereas at $t = 1.0$, it differs most strongly at large $t-t'$ values. This is a consequence of the fact that at early absolute times the system is in a dissipative equilibrium leading to the oldest prior memory being precisely that of the stationary friction with the static value $\gamma(-\infty)$. At later absolute times, the normalized kernel behaves as in case I, where the recent memory better reflects the stationary friction with the static value $\gamma(\infty)$.

The velocity autocorrelation functions are displayed in Figure 5 for all three cases. The dynamics of the chosen coordinate clearly changes during this irreversible change in the environment, and hence the iGLE represents a different class of dynamics than that which is seen with the stationary GLE's. The autocorrelation functions at the longest time displayed ($t = 4.0$) are all essentially the same, and this is indicative of the fact that they have all reached the same equilibrium. The early time autocorrelation function (at $t = -4.0$) is constant and exactly equal to 2 in case I, because in the ballistic regime the particle velocities are initialized according to the corresponding Boltzmann distribution. At the early times in cases II and III, the autocorrelation function has the structure of the equilibrium

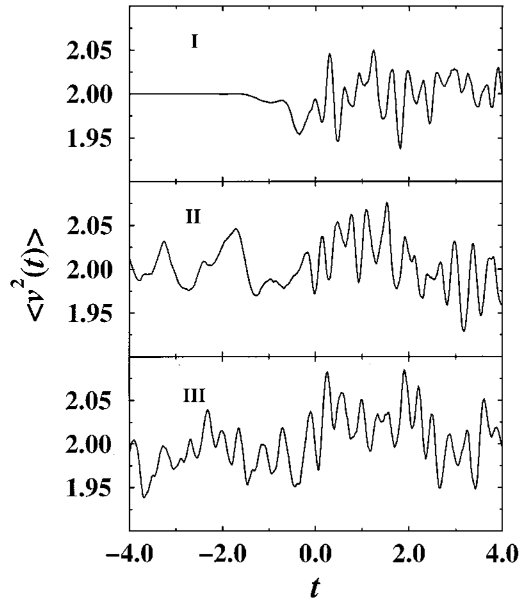

Figure 6. The mean square velocity $\langle v^2(t)\rangle$ is displayed for each of the cases as a function of time t. The curves in the top, middle, and bottom segments correspond to cases I, II, and III respectively.

dissipative systems with its respective stationary friction value $\gamma(-\infty)$. In all these cases, the autocorrelation functions at intermediate times do not exhibit a single simple correlation length and the correlation reduces toward that seen in the high friction limit.

The ($t = t'$) intercepts in Figure 5 all appear to be at or near the value of 2 corresponding to the value of k_bT under the current conditions. This is further underscored in Figure 6 which displays these intercepts as a function of absolute time t for all the cases. In the ballistic regime of case I, the equipartition relation holds exactly only because the initial conditions were chosen accordingly. It shows no fluctuations because at extremely low values of the coupling to the solvent the system energy is conserved. As the friction kernel becomes nonnegligible, however, the behavior of this case becomes similar to that of the others. In all the cases, the small fluctuations away from k_BT are a manifestation of the finite number of trajectories (10000) that are under investigation, i.e., finite-size effects. Note that the decay time in $\gamma(t,t')$ in these examples, as seen in Figures 3 and 4, is much longer than the time interval over which g is approximately constant. Thus these examples are generally far away from quasi-equilibrium. The fact that the equiparition is well-satisfied throughout these runs indicates that the iGLE is valid well beyond the equilibrium and quasi-equilibrium limits. Moreover, because the overall friction changes with time, the iGLEs also show a change in their dynamical behavior which is not seen in the usual GLE's.

V. Concluding Remarks

An iGLE has been constructed in which the stochastic dynamics are driven by an irreversible change in the response of the environment. The random force and the nonstationary friction kernel in this system satisfy a generalization of the fluctuation−dissipation relation, thus assuring that the system is consistent with the usual stationary GLE's in the equilibrium and quasi-equilibrium limits of the solvent. This has been further supported by numerical simulations of several parametrizations of a nonstationary friction kernel, in which the equipartition of energy is satisfied throughout the dynamics. These simulations also illustrate the non-stationary behavior in the autocorrelation functions of the chosen coordinate's velocity, extending the study of stochastic dynamics beyond the usual stationary cases.

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(35) A subtle point about the lower limit in the time integration of the iGLE is in order as it has been written implicitly throughout. In principle, the integration should be taken to the beginning of time, i.e., $t = -\infty$. In practice, however, it is sufficient to let the integration run back far enough such that the friction kernel has decayed to essentially zero. As long as this is integrated long enough so that the trajectories lead to equilibrium, there is no error. Such is the case for all of the simulations in this paper and paper 2 of this series.[21]