PHYSICAL REVIEW A VOLUME 40, NUMBER 2 JULY 15, 1989

Breakdown of the Brownian motion model in ultrafast dynamics

S.-B. Zhu, Surjit Singh, and G. W. Robinson
Picosecond and Quantum Radiation Laboratory, Texas Tech University, P.O. Box 4260, Lubbock, Texas 79409

(Received 1 March 1989)

When the motion of the surrounding heat bath particles is a slow coordinate, a "system" particle and its bath become dynamically coupled. A nonlinear Langevin (Fokker-Planck) equation is required to describe the stochastic process. In general, the steady-state distribution is not canonical. The rapid-motion effect, in association with the dynamical coupling among multimodes of the system, and the combined contributions from nonlinear and non-Markovian processes, cause a breakdown of the conventional Brownian motion theory. The discussion given in this paper puts previous computer-simulation results on a better theoretical foundation.

I. INTRODUCTION

Most theorists have addressed the dynamical problem of a particle having internal degrees of freedom (such as a molecule) in a condensed surrounding phase through use of a linear phenomenological Langevin (or Fokker-Planck) equation based on the Brownian motion model.[1-6] According to this model, the particle ("system") changes its configuration so slowly that the surrounding phase ("bath") can always readjust its positions and momenta to reach perfect thermal equilibrium with every configuration of the system. Recent computer molecular-dynamics (MD) simulations[7-11] have shown that the Brownian motion model may not give a correct description for particle dynamics that take place on a time scale short relative to the bath motions. This situation arises naturally in "barrier-crossing" problems[1] where the particle of interest is subjected to the influences of steep potentials *from sources other than those from the bath.* In such "reversed time scale" situations, nonlinear effects become important. To shed more light on this problem and to put the previous MD results on more solid theoretical ground, we further discuss the dynamics from a classical statistical-mechanics point of view. To present a balanced perspective, Sec. II briefly reviews the modern Brownian motion model of Okuyama and Oxtoby. In Sec. III we give a qualitative outline of an ultrafast motion model for the dynamics. Section IV introduces a detailed Hamiltonian portrait of the problem, Sec. V shows how this Hamiltonian can lead to a modified Langevin equation of motion for the particle, while Sec. VI presents a method for calculating the bipartite distribution functions through an associated Fokker-Planck-type equation. A summary of our conclusions is given in Sec. VII.

II. BROWNIAN MOTION MODEL

It is well known[12] that the mean-square velocity in any degree of freedom of a "free" Brownian particle, which is large and heavy, tends to the equipartition value,

$$\langle v^2(t)\rangle = k_B T/M + [\langle v^2(0)\rangle - k_B T/M]e^{-2t/\tau} , \quad (1)$$

where τ is the correlation time of the particle velocity. Such a system will eventually reach equilibrium, and, once attained, has a natural tendency to stay there.

Okuyama and Oxtoby[13] have extended Eq. (1) to the more general non-Markovian, nevertheless Brownian, situation for free diffusion:

$$\langle v^2(t)\rangle = k_B T/M + [\langle v^2(0)\rangle - k_B T/M]\chi^2(t) , \quad (2)$$

where

$$\chi(t) = \mathcal{L}^{-1}\frac{1}{s+\hat{\zeta}(s)} .$$

Here $\hat{\zeta}(s)$ is the friction in frequency space and $\mathcal{L}^{-1}$ denotes the inverse Laplace transform. Both Eqs. (1) and (2) show how the Brownian particle reaches the equilibrium stationary state. The relaxation of the Brownian particle is caused by the weak deflection of its trajectories in its collisions with the surrounding bath which is at equilibrium.[14]

III. ULTRAFAST MOTION MODEL

In contrast to the Brownian motion model, and corresponding MD methods that initiate the trajectories by fixing the system in a given configuration then equilibrating the surrounding bath,[15] we have used full MD calculations void of these approximations to simulate the system-bath dynamics in a correct and natural way. The resulting dynamical effects include the fact that, for non-Brownian or reversed time scale problems, the bath experiences a lag time in trying to reach equilibrium with each new configuration of the rapidly evolving system.

Non-Boltzmann situations may occur if the ratio of the time related to the duration of the interactions with respect to the time related to the relaxation process can no longer be neglected.[16] Probably the most important feature of the dynamical system under consideration, which distinguishes it from the Brownian motion problem, is the existence of internal structure. The reduced mass, shape, size, and internal energy of the system may all change during the dynamical process. The bath requires a finite time to equilibrate around each new configuration of the system. If the reduced mass of the system is small in comparison with the masses of the bath particles, or if the intramolecular barrier is steep in a certain region, the system changes its configuration so rapidly that the surrounding bath can no longer keep up with this rapid motion. As a result, both the system and the bath remain locally out of equilibrium with each other. This results in a temperature gradient along the dynamical barrier-crossing coordinate, and noncanonical distributions persist.[8,9,11]

To model this ultrafast motion analytically, we notice that the ensemble average of the coupling Hamiltonian between the system and heat bath is not only a function of the dynamical coordinate, an aspect which lies within the conventional Brownian motion model, but is also a function of the conjugate momentum (Ref. 11, also cf. Sec. IV). The Brownian motion model is based on the assumption that the surroundings respond extremely rapidly to the motion of the particle of interest. On this time scale, the Brownian particle can be treated as being "clamped." However, in the actual case, the dynamical motion of the barrier-crossing system induces a perturbation in the coupling Hamiltonian. The faster the system moves, the more positive is the perturbative coupling term. This additional contribution leads to mixed position-momentum terms in the effective Hamiltonian, and noncanonical distributions follow.

According to the classical theory of vibrations, Brownian motion is similar to oscillations about equilibrium, while rapid unstable barrier crossing is similar to oscillations in a moving frame. In the latter case, both the center of mass and the reduced mass of the oscillator can be considered to be time dependent, giving rise to mixed position-momentum terms in the effective Hamiltonian. Because of dynamical coupling between the system and the bath, and among the multimodes of the system, the barrier-crossing coordinate, while a normal coordinate for the free molecule, is generally not a normal coordinate when the system is immersed in the bath. Neither can it be transformed to a normal coordinate by a point transformation.[17]

IV. SYSTEM-BATH INTERACTIONS

A. One-dimensional model

Let us first consider the one-dimensional problem, where the system particle is a diatomic molecule. Newton's laws of motion are

$$m\frac{d^2r}{dt^2}=f_1+f_2\ , \tag{3}$$

$$M_1\frac{d^2R_1}{dt^2}=-\frac{\partial U(Q)}{\partial Q}-f_1\ , \tag{4}$$

$$M_2\frac{d^2R_2}{dt^2}=\frac{\partial U(Q)}{\partial Q}-f_2\ . \tag{5}$$

In these equations, m is the mass of an approaching particle, M_1 and M_2 are the masses of the particles comprising the diatomic molecule; r, R_1, and R_2 correspond to their positions; f_1 and f_2 are forces from interactions of the particle m with M_1 and M_2: and $U(Q)$ is the intramolecular potential with $Q=R_1-R_2$. For simplicity, assume the diatomic particles 1 and 2 are identical. Equations (3)–(5) can then be rewritten as

$$M\frac{d^2R_c}{dt^2}=-f_1-f_2\ , \tag{6}$$

$$\mu\frac{d^2Q}{dt^2}=-\frac{\partial U(Q)}{\partial Q}-(f_1-f_2)/2\ , \tag{7}$$

$$\lambda\frac{d^2q}{dt^2}=f_1+f_2\ , \tag{8}$$

where $M=M_1+M_2$, $1/\lambda=1/m+1/M$, $1/\mu=1/M_1+1/M_2$, $R_c=(M_1R_1+M_2R_2)/(M_1+M_2)$ is the position of the center of mass of the diatomic molecule, and $q\equiv r-R_c$. Expanding the interactions f_i ($i=1$ or 2) in a power series

$$f_i=\sum_{\nu=1} a_\nu(r-R_i)^\nu \tag{9}$$

one can write Eq. (8) in terms of the expansion coefficients

$$\lambda\frac{d^2q}{dt^2}=2a_1q+a_2(2q^2+Q^2/2)+\cdots\ . \tag{10}$$

It is clear from Eq. (10) that in the one-dimensional problem, if interactions between the pair of colliding particles are linear ($a_\nu=0$ for $\nu\geq 2$), one may treat the diatomic molecule as a single particle M located at the center of mass. Particle m vibrates harmonically with respect to particle M. This motion is not disturbed at all by the internal vibrational motion of the diatomic molecule. In other words, the collision occurs adiabatically. This picture also holds if we investigate a number of particles surrounding the diatomic molecule, the motions of these particles are all independent of the molecule's internal degrees of freedom, giving the conventional Brownian motion picture.[18] In this situation the bath remains at equilibrium no matter how rapidly the diatomic molecule vibrates. On the other hand, when the coupling Hamiltonian contains anharmonicity, the colliding molecules become dynamically coupled. In the special case where the internal vibrational motion is very slow relative to the collision event, a perturbation approach can be used.[19]

Formally integrating Eq. (10), we find that q depends on the history of the internal motion of the diatomic molecule. The collision becomes inelastic and nonadiabatic. In this situation, one obtains nonequilibrium solvation.[20,21] The effective system-bath interaction is not a potential function of a conservative force.

One may divide the system-bath ensemble into a number of subsystems. Each contains a group of bath particles surrounding a certain configuration of the system. At steady state, the net energy flux from the system to the bath equals zero. However, when the dynamical processes of the system are rapid in comparison with the bath motion, energy exchange between the system and bath becomes inefficient. Depending on its specific state, energy balance is not necessarily preserved for every subsystem. The dynamical system gains kinetic energy in some subsystems, while in others it loses energy. As far as an individual subsystem is concerned, the conditional distributions[22] are not canonical. A dynamical process involving a specific state of a subsystem can then occur from an abnormal distribution.

B. Multidimensional model

We now consider a two-dimensional model. Defining θ as the angle of inclination of the molecular axis with respect to q, we rewrite Eq. (10),

$$\lambda\frac{d^2q}{dt^2}=a_1[(q^2+Q^2/4-qQ\cos\theta)^{1/2}+(q^2+Q^2/4+qQ\cos\theta)^{1/2}]+a_2(2q^2+Q^2/2)+\cdots\ . \tag{11}$$

This more complicated form is a consequence of the coupling between the relevant dynamical modes, i.e., the barrier crossing coordinate (Q), and other internal modes of the system (e.g., rotational motion about θ). Evidently, even for a linear interaction, the motion of particle m is continuously interrupted by the internal vibrations of the system. One again obtains nonequilibrium solvation. This conclusion is clearly valid for a three-dimensional model, and consequently, for any real system.

In summary, we conclude that when a dynamical system possesses internal degrees of freedom, the bath motion is disturbed by the internal motions of the system. Conversely, the internal motions of the system are in the same way influenced by the bath motions. The configurational and velocity distributions of the neighboring bath particles are generally not canonical, except for motions where changes of the state of the dynamical system can be neglected during the course of collision. If the relevant frequency of the system dynamics is high, this influence also includes feedback from the previous dynamical behavior, another type of nonlinear effect.

C. Effective couplings

As discussed above, when anharmonicity exists in a one-dimensional model, or even when only linear interactions exist in a multidimensional model, the system and bath may depart locally from equilibrium. Deviations from the equilibrium state depend on the time scale of the dynamical motion of the system relative to that of the bath relaxation. The collisional process becomes nonadiabatic.[23]

Before introducing the concept of effective coupling, let us consider the one-dimensional classical Hamiltonian,

$$H=P^2/2\mu+U(Q)+M\dot{R}_c^{\,2}/2+\sum_{i=1}^{N}[U_{\rm SB}(q_i,R_c,Q)+p_i^2/2m]+\sum_{i<j}U_{BB}(q_i-q_j) \tag{12}$$

of the interactive system plus bath. Here, (Q,P) denotes a set of position coordinates and conjugate momenta of the system, and (q_i,p_i) $(i=1,2,\ldots,N)$ represent the same parameters for the bath. The system-bath interaction Hamiltonian in Eq. (12) does not contain the system momentum P explicitly. However, in the nonquilibrated bath, the position and momentum coordinates of its constituent particles are interrupted continuously by the system motion [cf. Eq. (10)], slow system motion and fast system motion having different effects. Consequently, the coordinate and momentum distribution functions of the nearby bath have dependencies on the system parameters.

It is sometimes convenient to treat the heat bath as if it had a small finite number of degrees of freedom,[24] in particular, as a single "particle" interacting with the system through the ensemble averaged force, or the *effective interaction*. In the rapid-motion model, this effective interaction is not a potential function of a conservative force, but rather is a function of both the coordinates and the conjugate momenta of the system. This type of coupling leads to a nonlinear Langevin equation (cf. Sec. V).

To explain the problem more specifically, we split the system-bath coupling Hamiltonian into a static part,

$$H_s=\sum_{i=1}^{N}[U_{\rm SB}(\bar{q}_i-R_c-Q/2)+U_{\rm SB}(\bar{q}_i-R_c+Q/2)]$$

and a dynamical part,

$$H_d=\sum_{i=1}^{N}[U_{\rm SB}(\Delta q_i-R_c-Q/2)+U_{\rm SB}(\Delta q_i-R_c+Q/2)]+\cdots\ .$$

Here $\bar{q}_i$ describe the positions that the bath particles would occupy if they were in perfect thermal equilibrium with the system, while Δq_i are deviations from $\bar{q}_i$ caused by the local nonequilibrium dynamics. The static part of the coupling is a genuine potential function and is no different from the coupling terms found by Lindenberg and co-workers[19] for an equlibrated bath, and used by others[25] in applications of the Brownian motion model to chemical reaction dynamics. This static portion may be determined by clamping the system in a certain configuration, then equilibrating the surrounding bath. On the other hand, the dynamical portion constitutes a correction term derived from the actual motion of the system, and from the rapid variations of its reduced mass, size, and shape. Inclusion of this dynamical contribution should give rise to important improvements in the theoretical assessment of ultrafast dynamical processes in solids and liquids. This part of the coupling Hamiltonian, being a function of both Q and P, leads as expected to a nonlinear Langevin equation.

V. NONLINEAR LANGEVIN EQUATION

By using a classical model of coupled harmonic oscillators and assuming the system-bath interaction to be static and linear in the bath coordinates, Lindenberg and her co-workers[19] have derived a quasilinear Langevin equation (LE) in which the memory kernel and the random forces have a dependence on the position coordinates of the system. This equation, though non-Markovian, still lies within the framework of equilibrium solvation ideas.

The specific form of the system-bath interaction affects dramatically both the potential terms and the dissipation terms in the final LE.[26] Including anharmonicity in the bath oscillators, treating the nonlinearities perturbatively, and using the adiabatic elimination technique,[27] Marchesoni[28] found that both the modified potential and the dissipation depend on the environmental temperature explicitly. By use of a "renormalization" procedure,[7] this temperature dependence is equivalent to a dependence on barrier height. These effects were also discovered in MD calculations.[8-11] Similar conclusions have been drawn analytically by Grigolini.[29] However, the analytical treatments were based on an equilibrium solvation view, which takes into account static system-bath coupling only. To extend these results, we notice that, in the nonequilibrium solvation regime, the distribution functions of the surrounding bath particles depend on the system motion. Thus the ensemble averages of random variables are functions of both the barrier-crossing coordinate and the corresponding momentum of the system. In this nonequilibrium case, the fluctuation-dissipation relation is generally not applicable, reminiscent of the case where a liquid is subjected to a rapidly oscillatory external field[30] or to a rapidly moving surface.[31] An alternative approach uses the concept of the effective coupling, which will be described in the following.

The locally nonequilibrated one-dimensional system and bath particles are modeled by the Hamiltonian

$$H=P^2/2\mu(Q)+U(Q)+p^2/2m+m\omega^2q^2/2-A(Q,P)q\ . \tag{13}$$

The last term is seen to represent dynamical coupling, and it is to be noted that the reduced mass of the system μ is, in general, a function of Q. For simplicity in manipulation, but without loss of generality, the interaction has been assumed to be linear in the bath particle coordinate. The Hamiltonian (13) is then similar to the IO (independent-oscillator) model of Ford, Lewis, and O'Connell.[32] One now writes the equations of motion,

$$\dot{P}=\frac{\partial A(Q,P)}{\partial Q}-\frac{\partial}{\partial Q}[U(Q)+P^2/2\mu(Q)]\ , \tag{14}$$

$$\dot{Q}=P/\mu(Q)-\frac{\partial A(Q,P)}{\partial P}q\ , \tag{15}$$

$$\dot{p}=A(Q,P)-\omega^2 q\ , \tag{16}$$

$$\dot{q}=p\ . \tag{17}$$

Formally integrating the bath coordinates and substituting the results into Eq. (14) yields the nonlinear LE

$$\dot{P}+\frac{\partial\tilde{U}(Q,P)}{\partial Q}-\int_0^t d\tau\,\zeta(Q,P;t-\tau)P(\tau)=\mathcal{F}(Q,P;t)\ . \tag{18}$$

In Eq. (18), the effective barrier potential is

$$\tilde{U}(Q,P)\equiv U(Q)+P^2/2\mu(Q)-A(Q,P)/2\omega^2\ , \tag{19}$$

the memory kernel is

$$\zeta(Q,P;t-\tau)=\frac{\partial A[Q(t),P(t)]}{\partial Q}\,\frac{\partial A[Q(\tau),P(\tau)]}{\partial Q}\times\left[1-\frac{\partial U(Q)/\partial Q}{\partial[P^2/2\mu(Q)]/\partial Q}\right]\frac{\cos\omega(t-\tau)}{\omega^2}\ , \tag{20}$$

and the random force is

$$\mathcal{F}(Q,P;t)=\frac{\partial A(Q,P)}{\partial Q}\left[\left[q(0)-\frac{A(Q_0,P_0)}{\omega^2}\right]\cos\omega t+\frac{p(0)}{\omega^2}\sin\omega t\right]\ . \tag{21}$$

This is, of course, not a rigorous derivation since we have merely asserted the form of the coupling $A(Q,P)$. In general, Eqs. (20) and (21) do not connect through the fluctuation-dissipation relation. Fluctuations in nonlinear systems can produce order.[33] They propagate unstable barrier dynamics to other regimes and transfer information from short- to long-time dynamics.[34]

The key points we want to make here are the following. (1) The rapid dynamical motions of the system cause the effective coupling Hamiltonian to take on a mixed form in P and Q. (2) This Hamiltonian further leads to a nonlinearity in the LE. (3) Inclusion of anharmonicity in the bath oscillator causes additional nonlinearity. (4) The effective barrier potential, and consequently entropy effects, depends not only on Q but also on P. (5) The variation of reduced mass with respect to the coordinate Q gives rise to an additional contribution to the effective barrier potential, a nonlinear effect first described in Ref. 10. (6) Another nonlinear effect concerns the memory kernel, which, from Eq. (20), itself depends on the system parameters including the barrier potential.[8,11]

VI. STATIONARY DISTRIBUTION FUNCTION

A. Brownian motion

The general form of the Fokker-Planck equation (FPE) reads

$$\frac{\partial\rho(Q,P;t)}{\partial t}=\sum_{r=0}\Gamma_r\rho(Q,P;t)\ , \tag{22}$$

where $\rho(Q,P;t)$ represents the reduced distribution function in the relevant phase space of the system under study, and Γ_r denote the perturbation terms of order r in the corresponding FP operator. Assuming the coupling to be static and linear in the bath coordinates, Marchesoni[28] derived the FP operators for $r=0$, 1, and 2. The Markovian assumption is implicit in the truncation of the series to order $r=1$. In this approximation, Eq. (22) is sometimes called the Kramers-Fokker-Planck equation. This leads to the ordinary LE.

At steady state, $\partial\rho(Q,P;t)/\partial t=0$. A particular solution of this steady-state FPE in lowest order is the canonical distribution, which is valid only under the condition

$$k_B T \frac{\partial \rho(Q,P)}{\partial P} + P/M = 0 \ . \tag{23}$$

In other words, if the stable velocity distribution is Maxwellian at every position of the system, the configurational distribution must then be canonical regardless of the friction. This conclusion is true even for the much more complicated second-order ($r=2$) FPE. Keep in mind that Eq. (23) is obtained only when the dynamical effects of the system motion can be neglected.

The one-dimensional diffusion problem of two interacting Brownian particles in a periodic potential was investigated by Vollmer.[35] The probability distribution $\rho(Q,P,R_c,P_c;t)$ describing this stochastic process is a solution of the FPE:

$$\frac{\partial \rho(Q,P,R_c,P_c;t)}{\partial t} + \left[P_c/M \frac{\partial}{\partial R_c} + P/\mu \frac{\partial}{\partial Q} - \frac{\partial}{\partial P_c}(\zeta P_c/\mu) - \frac{\partial}{\partial P}\left[\zeta P/\mu + \frac{\partial \tilde{U}(Q)}{\partial Q}\right] - \zeta \langle P_c^2/\mu \rangle \frac{\partial^2}{\partial P_c^2} - \zeta \langle P^2/\mu \rangle \frac{\partial^2}{\partial P^2} \right] \rho(Q,P,R_c,P_c;t) = 0 \ , \tag{24}$$

where P_c is the translational momentum of the diatomic system. If Q and R_c are normal coordinates, that is, if the vibrational mode and the translational mode are not dynamically coupled, the stationary solution of Eq. (24) is

$$\rho(Q,P,R_c,P_c) = c \exp\{ -[P_c^2/\langle P_c^2 \rangle + P^2/\langle P^2 \rangle + \tilde{U}(Q)/\langle \tilde{U}(Q) \rangle]\} \ .$$

As expected, this is the Boltzmann distribution.

B. Ultrafast motion

In a recent paper, Masters[36] reviewed the assumptions made in the ordinary Langevin, Smoluchowski, and lowest-order FPE's, and found that the validity of these reduced equations, which simply attempt to describe the motion of the Brownian particle alone, relies on separations of time scales. In particular, the Smoluchowski equation requires that $\tau_Q \gg \tau_p$, whereas the Fokker-Planck and LE require that $\tau_Q, \tau_p \gg \tau_f$, where τ_Q, τ_p, and τ_f represent, respectively, the correlation times for the particle position, velocity, and total force exerted on the particle by the bath. These conditions may not be satisfied when large forces from sources other than those from the bath are present.

Starting from the classical Hamiltonian in Eq. (12), Lebowitz and Rubin[37] have derived a FPE for a Brownian particle,

$$\frac{\partial \rho(Q,P;t)}{\partial t} + \left[\frac{P\partial}{\mu \partial Q} - \frac{\partial \tilde{U}(Q)}{\partial Q}\frac{\partial}{\partial P} - \zeta \left[\langle P^2/\mu \rangle \frac{\partial^2}{\partial P^2} + \frac{1}{\mu}\frac{\partial}{\partial P} P \right] \right] \times \rho(Q,P,t) = O(\gamma^3) \ , \tag{25}$$

where $\gamma = (m/M)^{1/2}$ is a measure of the dynamical effects induced by the motion of the Brownian particle. If the ratio γ is not very small, the higher-order contributions of the dynamical motion of the system become non-negligible, especially when there exists a position-dependent external force field which causes spatial nonuniformity.[38–40] Steady state is attained as a result of the competition between the pumping process caused by the external force (or the periodic variation of the internal energy of the system) and energy exchange through system-bath interactions. One obtains noncanonical distributions in this case. By use of a perturbation method, where the distribution function is split into an unperturbed (canonical) component and a perturbed component, Lebowitz and Rubin[37] further found that the distortion of the canonical distribution caused by the dynamical motion of the particle becomes larger when the external force becomes larger and the bath friction becomes lower. This is completely in accord with the MD results.[11] However, in the approach of Lebowitz and Rubin, the position-dependent friction caused by the nonlinear system-bath interaction has not been taken into account. Influences of the variations of the reduced mass, size, and shape on the dynamics have been ignored. The process is purely Markovian.

In a more general nonlinear, non-Markovian situation, the effects of nonequilibrium solvation become significant. One obtains a nonlinear FPE which is equivalent to the nonliner LE (18). A rigorous derivation seems not feasible. However, using the technique constructed by Novikov[41] and by Miguel and Sancho,[42] one may derive a generalized FPE. This generalized FPE reduces to the Ito-Stratonivich[43,44] type of stochastic differential equation in the Markovian limit, and further reduces to the ordinary Kramers-Fokker-Planck equation by omitting the nonlinearity. In linear, non-Markovian dynamics, this then becomes equivalent to the generalized Smoluchowski equation derived by Okuyama and Oxtoby.[13] It is evident that the steady-state solution of the nonlinear FPE is generally not canonical. Its integration (e.g., the mean kinetic energy) cannot be a constant along the barrier-crossing coordinate.

The above treatments are all limited to the one-dimensional problem. On the other hand, almost every dynamical process in the liquid state, even the simplest, includes multimodes. The coupling among these modes gives rise to additional contributions to the potential, which then perturb the FPE.[45] In addition, since nonequilibrium solvation acts on the motions of each mode, this coupling is generally dynamical (cf. Sec. IV). Because of these dynamical couplings, the modified coordinates of the system are not normal coordinates.[9] Moreover, the internal structure, reduced mass, shape, and size of the system vary during the dynamical process. These extra complications further perturb the Fokker-Planck operator nonlinearly.

C. Boltzmann equation

Probably a better approach to such complicated problems is provided by the Boltzmann equation. The nonlinearity is embodied in the collision operator

$$\left[\frac{\partial\rho}{\partial t}\right]_{\mathrm{col}}=\int d^3q\int d^3p\,\sigma(Q,P,R_c,P_c;q,p\,|\,Q',P',R_c',P_c';q',p')|P/m -P_c/M|[\rho(Q',P';t)f(Q',P',q',p';t)-\rho(Q,P;t)f(Q,P,q,p;t)]\ , \tag{26}$$

where $\sigma(Q,P,R_c,P_c;q,p\,|\,Q',P',R_c',P_c';q',p')$ is the differential scattering cross section[38] of the colliding pair described in Sec. IV, and $f(Q,P,q,p,t)$ represents the distribution function of the bath particles. These quantities have mixed forms of the positions and momenta, since the kinetic energy and the total momentum are not conserved during the course of collision. As a result, deviations from the canonical distribution become inevitable. The collision operator may be linearized for certain processes. For example, a system in which one particle is very large and very heavy compared with others (i.e., a Brownian particle) gives rise to a linear equation for this particle.[46] This equation then reduces to the ordinary FPE.[5,47]

VII. CONCLUSIONS

Because of its internal structure, a real particle is generally different from a Brownian particle. When the bath motion becomes a slow coordinate, such as in the nonadiabatic frozen solvent situation,[48] the system and the heat bath become dynamically coupled. This is in addition to the static coupling of ordinary Brownian motion theory. In addition, couplings among the multimodes of the system because of nonequilibrium solvation are also dynamical.[49] These dynamical aspects, in association with joint contributions from nonlinear and non-Markovian effects, cause a breakdown of the conventional Brownian motion theory. Instead, the rapid-motion model introduced here is demanded. The dynamical coupling Hamiltonian, having a mixed P and Q dependence, leads to a nonlinear LE and FPE. Application of these more general equations to ultrafast dynamical processes in liquids or solids is essential. In fact, the rapid-motion model has successfully interpreted all the phenomena thus far observed in MD calculations of barrier crossing. For example, Eq. (19) indicates a P-dependent effective barrier potential (more rigorously, this is not a genuine potential since the corresponding force is not conservative), as observed in Ref. 10. On the other hand, Eq. (20) shows that the memory kernel itself is a function of P, in line with the discovery in Ref. 8. Equations (25) (in particular with P-dependent ζ) and (26) predict a locally noncanonical velocity distribution. This is exactly what was found in Refs. 9 and 11 and more recently in Ref. 50. The rapid-motion should also be applicable to various types of ultrafast dynamics in the liquid state, including chemical reactions. The resulting complications will include local nonequilibrium and noncanonical distributions along the bare barrier-crossing coordinate,[50] the barrier potential dependences of entropy effects, and the effects of system characteristics on the time-dependent friction. These features have been neglected in past work. They lie outside the framework of the Brownian motion model and linear Langevin or Fokker-Planck equations.

ACKNOWLEDGMENTS

Financial support at the PQRL has been shared by the Robert A. Welch Foundation (D-0005 and D-1094), the National Science Foundation (CHE8611381), and the State of Texas Advanced Research Program (1306).

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