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Uses and Abuses of the Langevin Equation for Chemical Reactions in Condensed Phases

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The Langevin and Fokker–Planck equations are useful in the description of many classical and quantum mechanical systems. However, these equations are justifiable from molecular considerations under very restricted conditions. These conditions include weak coupling, Brownian motion, and systems with special Hamiltonians. The application of these equations to chemical reactions in condensed phases is fraught with peril, particularly for fluid systems. We examine the molecular derivations of these equations and describe the conditions under which they are justifiable. It is, of course, possible that the equations are useful under other conditions.

KEY WORDS: Langevin equation; Fokker–Planck equation; chemical reactions; weak coupling; Brownian motion.

1. INTRODUCTION

There have been many attempts to derive the Langevin and Fokker–Planck equations from molecular considerations[(1–3)] since they were introduced in a heuristic fashion by the original investigators. There have also been many caveats raised for the application of these equations and it has been demonstrated that careless use of these equations leads to incorrect results.[(4,5)] In this paper, we shall restrict our attention to classical systems, although the extensions to quantum systems is straightforward in many cases.

The overall systems that we consider have the following properties in common. They consist of a system of a few degrees of freedom described by a Hamiltonian H_s. The isolated system does not relax to equilibrium and

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it is assumed that the dynamical equations of the system can be solved. The motion of the isolated system is characterized by a time scale τ_s. The system is embedded in a bath of many degrees of freedom with Hamiltonian H_b. The isolated bath will decay to equilibrium on a short time scale τ_b in the sense that its macroscopic properties can be obtained by using an equilibrium distribution function. Finally, the interaction between the system and the bath is described by a potential ϕ. This interaction stimulates the decay of the system to equilibrium on a time scale τ_R.

The coordinates and momenta of the system will be denoted by $\mathbf{R}$ and $\mathbf{P}$ and those of the bath by $\mathbf{r}$ and $\mathbf{p}$. Thus, $H_s = H_s(\mathbf{R}, \mathbf{P})$, $H_b = H_b(\mathbf{r}, \mathbf{p})$, and $\phi = \phi(\mathbf{r}, \mathbf{R})$. We note that other variables, e.g., action–angle variables,(6) may be useful in the description of some applications.

The interaction terms in the dynamical equations for the time dependence of a dynamical variable of the system $G(\mathbf{R}, \mathbf{P})$ and for the reduced distribution function for the system $W(\mathbf{R}, \mathbf{P}, t)$ involve time integrals over a time-dependent correlation function of fluctuating forces $\mathbf{K}$, where the average in the correlation function is over the bath degrees of freedom. Our criteria for the utility of the Langevin or Fokker–Planck approach is that this correlation function is either independent of the system variables or at most depends on the time evolution of these variables under the Hamiltonian H_s. If this is not true, little has been accomplished by forcing the equations into a Langevin or Fokker–Planck form.

In Section 2, we present exact equations of motion for an arbitrary dynamical variable $G(\mathbf{R}, \mathbf{P})$ and for the reduced distribution function $W(\mathbf{R}, \mathbf{P}, t)$. These equations are obtained using projection operator techniques and are rewritings of the usual equations in suggestive forms. In Section 3, we describe the conditions under which our criteria of validity are met. In Section 4, we investigate the conditions under which these simplified equations are valid for chemical reactions in condensed phases. Finally, in Section 5 we present a summary and conclusions.

2. DERIVATION OF EXACT DYNAMICAL EQUATIONS

The exact dynamical equations for $G(\mathbf{R}, \mathbf{P})$ and $W(\mathbf{R}, \mathbf{P}, t)$ can be rewritten in suggestive forms using projection operator techniques.

We consider a classical overall system consisting of a system with n degrees of freedom and a bath of N degrees of freedom with $n \ll N$. The Hamiltonian for the overall system is

$$H = H_s(\mathbf{R}, \mathbf{P}) + H_b(\mathbf{r}, \mathbf{p}) + \phi(\mathbf{r}, \mathbf{R}) \tag{2.1}$$

and the corresponding Liouville operator is

$$L = L_s(\mathbf{R}, \mathbf{P}) + L_b(\mathbf{r}, \mathbf{p}) + L_I(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) \tag{2.2}$$

where

$$L_s = \frac{\partial H_s}{\partial \mathbf{P}} \cdot \frac{\partial}{\partial \mathbf{R}} - \frac{\partial H_s}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{P}} \tag{2.3a}$$

$$L_b = \frac{\partial H_b}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{\partial H_b}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \tag{2.3b}$$

and

$$L_I = -\frac{\partial \phi}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{P}} - \frac{\partial \phi}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \tag{2.3c}$$

The projection operator that we use to obtain the dynamical equation for G is$^{(2)}$

$$PB = \int \tilde{\rho} B \, dX_b = \langle B \rangle \tag{2.4}$$

where B is an arbitrary dynamical variable, X_b is the phase point of the bath, and $\tilde{\rho}$ is the equilibrium conditional distribution function for the bath in the presence of a fixed system, i.e.,

$$\tilde{\rho} \equiv \rho_e / W_e = \rho_b e^{-\beta\phi} e^{\beta w} \tag{2.5}$$

where ρ_e is the equilibrium distribution function for the overall system, W_e is the reduced equilibrium distribution function for the system, ρ_b is the equilibrium distribution function for the isolated bath, and $w(\mathbf{R})$ is the potential of mean force, which is given by

$$e^{-\beta w} \equiv \langle e^{-\beta\phi} \rangle_0 \equiv \int \rho_b e^{-\beta\phi} \, dX_b \tag{2.6}$$

Thus, $\tilde{\rho}$ is a function of $\mathbf{r}$, $\mathbf{p}$, and $\mathbf{R}$ and is normalized by

$$\int \tilde{\rho} \, dX_b = 1 \tag{2.7}$$

We define the fluctuating force $K_G(t)$ by

$$\begin{aligned} K_G(t) &\equiv e^{(1-P)Lt}(1-P)\, LG \\ &= e^{(1-P)Lt}(1-P)\, \dot{\mathbf{P}} \cdot \nabla_P G = -e^{(1-P)Lt}(\nabla_R(\phi - w) \cdot \nabla_P G) \end{aligned} \tag{2.8}$$

and use standard procedures to obtain$^{(7)}$

$$\dot{G}(t)=[(\nabla_P H_s\cdot\nabla_R-\nabla_R H_s\cdot\nabla_P-\nabla_R w\cdot\nabla_P)\,G](t)$$
$$+\int_0^t e^{L(t-\sigma)}(\nabla_P-\beta\nabla_P H_s)\cdot\langle\mathbf{K}K_G(\sigma)\rangle\,d\sigma+K_G(t) \qquad (2.9)$$

Equation (2.9) is an exact equation for $G(t)$. It has a form suggestive of the Langevin equation, since $K_G(t)$ is a fluctuating force with properties

$$\langle K_G(t)\,B(\mathbf{R},\mathbf{P})\rangle=\langle K_G(t)\rangle\,B(\mathbf{R},\mathbf{P})=0 \qquad (2.10)$$

where B is an arbitrary dynamical variable of the system. Note that if G is a nonlinear function of $\mathbf{P}$, $K_G(t)$ involves system variables and is, at best, multiplicative. The notation $[\cdot](t)$ denotes the value of the quantities in the bracket at time t evolving under the full Liouville operator and

$$\mathbf{K}(t)\equiv e^{(1-P)Lt}(1-P)\,L\mathbf{P}=-e^{(1-P)Lt}\,\nabla_R(\phi-w) \qquad (2.11)$$

is the fluctuating force conjugate to the momentum. The correlation function in Eq. (2.9) is, in general, a complicated function of $\mathbf{R}$, $\mathbf{P}$, and σ.

The projection operator that is used to obtain an equation for $W(\mathbf{R},\mathbf{P},t)$ is $\hat{P}$,$^{(1)}$ where

$$\hat{P}B=\tilde{\rho}\int dX_b\,B \qquad (2.12)$$

which corresponds to P, but acts in the dual space. We use the Liouville equation for the time-dependent distribution function of the overall system $\rho(t)$,

$$\dot{\rho}(t)=-L\rho(t) \qquad (2.13)$$

and introduce the quantities

$$y(t)\equiv\hat{P}\rho(t)=\tilde{\rho}W(t) \qquad (2.14a)$$
$$z(t)\equiv(1-\hat{P})\,\rho(t)\equiv\hat{Q}\rho(t) \qquad (2.14b)$$

with properties

$$\begin{aligned}&\int y(t)\,dX_b=W(t)\\&\int z(t)\,dX_b=0\end{aligned} \qquad (2.15)$$

to obtain an exact equation for $\dot{W}(t)$ in the form$^{(1)}$

$$\begin{aligned}\dot{W}(\mathbf{R}, \mathbf{P}, t) = {} & \left(-\frac{\partial H_s}{\partial \mathbf{P}} \cdot \frac{\partial}{\partial \mathbf{R}} + \frac{\partial H_s}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{P}} + \frac{\partial w}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{P}} \right) W(\mathbf{R}, \mathbf{P}, t) \\ & + \nabla_P \cdot \int dX_b \, \widehat{\nabla_R \phi} e^{-\hat{Q}L\hat{Q}t} z(0) \\ & + \nabla_P \cdot \int_0^t d\sigma \int dX_b \, \{ \widehat{\nabla_R \phi} \exp[-\hat{Q}L\hat{Q}\sigma] \, \tilde{\rho} \, \widehat{\nabla_R \phi} \} \\ & \cdot (\nabla_P + \beta \nabla_P H_s) \, W(\mathbf{R}, \mathbf{P}, t - \sigma) \end{aligned} \tag{2.16}$$

Here,

$$\widehat{\nabla_R \phi} \equiv \nabla_R \phi - \langle \nabla_R \phi \rangle = \nabla_R (\phi - w) \tag{2.17}$$

Equation (2.16) contains a streaming term, an initial value term involving $z(0)$, and a term involving a time integral. It has a form suggestive of the Fokker–Planck equation. Since Eqs. (2.9) and (2.16) are exact, they are equivalent in the sense that total averages of $G(t)$ obtained from these equations are identical.

3. SIMPLIFICATION OF THE EXACT EQUATIONS OF MOTION

In this section we study the conditions under which Eq. (2.9) becomes a generalized Langevin equation and Eq. (2.16) becomes a generalized Fokker–Planck equation. In general the three time scales τ_s, τ_b, and τ_R are arbitrary and we cannot expect simplifications of these equations, except in special cases, unless $\tau_R \gg \tau_b$.

3.1. Weak Coupling$^{(3)}$

In an overall system in which the system is weakly coupled to the bath, we can introduce a smallness parameter λ to rewrite Eqs. (2.1) and (2.2) as

$$H = H_s + H_b + \lambda \phi \qquad \text{and} \qquad L = L_s + L_b + \lambda L_I \tag{3.1}$$

In addition, w is proportional to λ, as are $\mathbf{K}$ and K_G. In Eq. (2.9), there is a factor of λ in front of the $\nabla_R w \cdot \nabla_P$ term and the $K_G(t)$ term and a factor of λ^2 in front of the time integral. If the correlation function in Eq. (2.9) decays on a $\lambda^0 = 1$ time scale, it becomes to order λ^2

$$\lambda^2 \langle \mathbf{K} K_G(\sigma) \rangle = \lambda^2 \langle [(1 - P_0) \nabla_R \phi] \, e^{L_0 \sigma} (1 - P_0) \nabla_R \phi \rangle_0 \cdot \nabla_P G \tag{3.2}$$

where $L_0 \equiv L_b + L_s$, the average is over ρ_b,

$$P_0 B = \langle B \rangle_0 \tag{3.3}$$

and

$$P_0 L_0 (1 - P_0) B = 0 \tag{3.4}$$

Equation (3.2) can be rewritten

$$\begin{aligned} \lambda^2 \langle \mathbf{K} K_G(\sigma) \rangle = \lambda^2 \langle [(1 - P_0)\, \nabla_R \phi(\mathbf{r}, \mathbf{R})](1 - P_0) \\ \times \nabla_{R0(\sigma)} \phi(\mathbf{r}_0(\sigma), \mathbf{R}_0(\sigma)) \rangle_0 \, e^{L_s \sigma} \nabla_P G \end{aligned} \tag{3.5}$$

where

$$\mathbf{r}_0(\sigma) \equiv e^{L_0 \sigma} \mathbf{r} = e^{L_b \sigma} \mathbf{r}, \qquad \mathbf{R}_0(\sigma) \equiv e^{L_0 \sigma} \mathbf{R} = e^{L_s \sigma} \mathbf{R} \tag{3.6}$$

The correlation function is still a function of $\mathbf{R}$ and $\mathbf{R}_0(\sigma)$, and $e^{L_s \sigma} \nabla_P G$ is a function of $\mathbf{R}_0(\sigma)$ and $\mathbf{P}_0(\sigma)$. We denote the correlation function by $\mathsf{C}(\mathbf{R}, \mathbf{R}_0(\sigma), \sigma)$ and $e^{L_s \sigma} \nabla_P G$ by $\mathbf{J}(\mathbf{R}_0(\sigma), \mathbf{P}_0(\sigma))$. We must still operate on Eq. (3.5) by $\nabla_P - \beta \nabla_P H_s$. The result is

$$\begin{aligned} &(\nabla_P - \beta \nabla_P H_s) \cdot \mathsf{C}(\mathbf{R}, \mathbf{R}_0(\sigma), \sigma) \cdot \mathbf{J}(\mathbf{R}_0(\sigma), \mathbf{P}_0(\sigma)) \\ &\quad = [\nabla_P \mathbf{R}_0(\sigma) \cdot \nabla_{R0(\sigma)} \cdot \mathsf{C}] \cdot \mathbf{J} \\ &\qquad + \mathsf{C}^\dagger \colon (\nabla_P \mathbf{R}_0(\sigma) \cdot \nabla_{R0(\sigma)} + \nabla_P \mathbf{P}_0(\sigma) \cdot \nabla_{P0(\sigma)}) \mathbf{J} - \beta \nabla_P H_s \cdot \mathsf{C} \cdot \mathbf{J} \end{aligned} \tag{3.7}$$

The last term in Eq. (3.7) involves $\nabla_P H_s$, which can be written

$$\nabla_P H_s = \nabla_P H_s(\sigma) = \nabla_P \mathbf{R}_0(\sigma) \cdot \nabla_{\mathbf{R}0(\sigma)} H_s(\sigma) + \nabla_P \mathbf{P}_0(\sigma) \cdot \nabla_{P0(\sigma)} H_s(\sigma) \tag{3.8}$$

Finally, the term $e^{L(t - \sigma)}$ can be approximated by

$$e^{L(t - \sigma)} = e^{Lt} e^{-L\sigma} \approx e^{Lt} e^{-L_0 \sigma} \tag{3.9}$$

When this operates on (3.7) we obtain

$$\begin{aligned} &e^{Lt} [(e^{-L_s \sigma} \nabla_P \mathbf{R}_0(\sigma)) \colon (\nabla_R \mathsf{C}) \cdot \mathbf{J}(\mathbf{R}, \mathbf{P}) \\ &\quad + \mathsf{C}^\dagger \colon ([e^{-L_s \sigma} \nabla_P \mathbf{R}_0(\sigma)] \cdot \nabla_R \mathbf{J}(\mathbf{R}, \mathbf{P}) + [e^{-L_s \sigma} \nabla_P \mathbf{P}_0(\sigma)] \cdot \nabla_P J(\mathbf{R}, \mathbf{P})) \\ &\quad - \beta ([e^{-L_s \sigma} \nabla_P \mathbf{R}_0(\sigma)] \cdot \nabla_R H_s + [e^{-L_s \sigma} \nabla_P \mathbf{P}_0(\sigma)] \cdot \nabla_P H_s) \cdot \mathsf{C} \cdot \mathbf{J}(\mathbf{R}, \mathbf{P})] \end{aligned} \tag{3.10}$$

Here, $\mathsf{C} = \mathsf{C}(\mathbf{R}_0(-\sigma), \mathbf{R}, \sigma)$ and $\nabla_R \mathsf{C}$ acts on $\mathbf{R}$ only. This is a complicated expression, but it satisfies the criterion that the integral over σ involves the

σ dependence of $\mathbf{r}_0(\sigma)$ and expressions like $[e^{-L_s\sigma}\nabla_P \mathbf{R}_0(\sigma)]$, which involve the dynamics of the isolated system.

Equation (3.10) simplifies under some additional conditions. If $G(\mathbf{R}, \mathbf{P}) = \mathbf{P}$, $\mathbf{J} = \mathsf{I}$, and the terms involving derivatives of $\mathbf{J}$ disappear. If the interaction between the system and the bath is linear in the system coordinate, $\nabla_R \phi$ is independent of $\mathbf{R}$ and the derivative of C disappears. If the interaction between the system and the bath depends on $\mathbf{r} - \mathbf{R}$, C depends on $\mathbf{R} - \mathbf{R}_0(-\sigma)$ and σ. Finally, if the system Hamiltonian is that of a harmonic oscillator, then, e.g.,

$$e^{-L_s\sigma}\nabla_P \mathbf{P}_0(\sigma) = \mathsf{I}\cos \Omega\sigma \tag{3.11}$$

Note that even in the simplified form we need to know $\mathsf{C}(\sigma)$ as a function of σ rather than its time integral.

In the weak coupling limit the equation for $\dot{W}(\mathbf{R}, \mathbf{P}, t)$, Eq. (2.16), also simplifies. There is a λ in front of the $\partial w/\partial \mathbf{R}$ term and in front of the initial value term. A factor of λ^2 appears in front of the term involving a time integral. Again, the integral can be computed to order λ^0. It becomes

$$\begin{aligned}
&\nabla_P \cdot \int dX_b \, ([(1-P_0)\nabla_R \phi]\, e^{-L_0\sigma} \rho_b [(1-P_0)\nabla_R \phi] \\
&\qquad \cdot (\nabla_P + \beta\nabla_P H_s)\, e^{+L_s\sigma} W(\mathbf{R}, \mathbf{P}, t)) \\
&\quad = \nabla_P \cdot \mathsf{C}(\mathbf{R}, \mathbf{R}_0(-\sigma), -\sigma) \cdot e^{-L_s\sigma}(\nabla_P + \beta\nabla_P H_s)\, e^{L_s\sigma} W(\mathbf{R}, \mathbf{P}, t)
\end{aligned} \tag{3.12}$$

Using the same considerations as above in the simplification of the Langevin equation, we can obtain

$$\begin{aligned}
&\nabla_P \cdot \mathsf{C}(\mathbf{R}, \mathbf{R}_0(-\sigma), -\sigma) \cdot e^{-L_s\sigma}(\nabla_P + \beta\nabla_P H_s)\, e^{L_s\sigma} W(\mathbf{R}, \mathbf{P}, t) \\
&\quad = \nabla_P \mathbf{R}_0(-\sigma) : \nabla_{\mathbf{R}_0(-\sigma)} \mathsf{C}(\mathbf{R}, \mathbf{R}_0(-\sigma), -\sigma) \\
&\qquad \cdot \{[e^{-L_s\sigma}\nabla_P \mathbf{R}_0(\sigma)] \cdot (\nabla_R + \beta\nabla_R H_s) \\
&\qquad + [e^{-L_s\sigma}\nabla_P \mathbf{P}_0(\sigma)] \cdot (\nabla_P + \beta\nabla_P H_s)\}\, W(\mathbf{R}, \mathbf{P}, t) \\
&\qquad + \mathsf{C}^{\dagger}(\mathbf{R}, \mathbf{R}_0(-\sigma), -\sigma) : \nabla_P \{\cdot\}\, W(\mathbf{R}, \mathbf{P}, t)
\end{aligned} \tag{3.13}$$

where the expression in $\{\cdot\}$ in the last term in Eq. (3.13) is identical to the expression in $\{\cdot\}$ in the first term on the rhs. Further simplifications occur under the conditions described above for the Langevin equation. Even in the simplest form, we must know C as a function of σ.

3.2. Brownian Motion$^{(1,2,7)}$

If all the changes in the motion of the system are slow because, e.g., its mass M is large compared to the mass of a bath particle m and its momentum is large compared to the momentum of a bath particle, i.e.,

$$|P| = \left(\frac{M}{m}\right)^{1/2} |p| \equiv \varepsilon^{-1} |p| \tag{3.14}$$

where ε is defined by Eq. (3.14), it is useful to introduce the momentum

$$\mathbf{P}^* = \varepsilon \mathbf{P}$$

which is of order ε^0. Equation (2.9) becomes

$$\begin{aligned}\dot{G}(\mathbf{R}(t), \mathbf{P}^*(t)) = {} & \varepsilon[(\nabla_{P*} H_s \cdot \nabla_R - \nabla_R H_s \cdot \nabla_{P*} - \nabla_R w \cdot \nabla_{P*}) G](t) \\ & + \varepsilon^2 \int_0^t e^{L(t-\sigma)} (\nabla_{P*} - \beta \nabla_{P*} H_s) \cdot \langle \mathbf{K} K_G(\sigma) \rangle \, d\sigma + \varepsilon K_G(t)\end{aligned} \tag{3.15}$$

where

$$K_G(t) = -e^{(1-P)Lt} \nabla_R(\phi - w) \cdot \nabla_{P*} G \tag{3.16}$$

Equation (2.2) becomes

$$L = \varepsilon L_s(\mathbf{R}, \mathbf{P}^*) + L_b(\mathbf{r}, \mathbf{p}) - \varepsilon \nabla_R \phi \cdot \nabla_{P*} - \nabla_r \phi \cdot \nabla_p \tag{3.17}$$

and

$$L_s(\mathbf{R}, \mathbf{P}^*) = \nabla_{P*} H_s \cdot \nabla_R - \nabla_R H_s \cdot \nabla_{P*} \tag{3.18}$$

Since there is a factor of ε^2 in front of the time integral in Eq. (3.15), the kernel can be simplified to

$$\langle \mathbf{K} K_G(\sigma) \rangle = \langle [\nabla_R(\phi - w)] \, e^{\tilde{L}_b \sigma} [\nabla_R(\phi - w)] \rangle \cdot \nabla_{P*} G \equiv \mathbf{C}(\mathbf{R}, \sigma) \cdot \nabla_{P*} G \tag{3.19}$$

where

$$\tilde{L}_b = L_b - \nabla_r \phi \cdot \nabla_p \tag{3.20}$$

and the average in Eq. (3.19) is taken over $\tilde{\rho}$, Eq. (2.5). This average is in general a function of $\mathbf{R}$. This simplification occurs if $\mathbf{C}$ decays to 0 on a molecular time scale. The time integral in Eq. (3.15) becomes

$$\int_0^t d\sigma \, \mathbf{C}^\dagger(\mathbf{R}(t), \sigma) \colon [(\nabla_{P*} - \beta \nabla_{P*} H_s) \nabla_{P*} G](t) \tag{3.21}$$

The kernel becomes independent of $\mathbf{R}$ if the interaction potential is a function of $\mathbf{r}-\mathbf{R}$.

For times $t>\tau_b$, the time integral in (3.21) can be extended to infinity and we do not need to know the σ dependence of C.

Equation (2.16) also simplifies under these conditions for the reduced system distribution function $W(\mathbf{R}, \mathbf{P}^*, t)$. In this equation, $\mathbf{P}$ is replaced by $\mathbf{P}^*$ and there is a factor of ε in front of the streaming and initial value terms and a factor of ε^2 in front of the time integral. The kernel in Eq. (2.16) becomes

$$\langle \widehat{\nabla_R \phi} e^{-\tilde{L}_b \sigma} \widehat{\nabla_R \phi} \rangle = \mathsf{C}(\mathbf{R}, \sigma) \tag{3.22}$$

and the last term in Eq. (2.16) becomes

$$\varepsilon^2 \int_0^t d\sigma\, \mathsf{C}^\dagger(\mathbf{R}, \sigma) \colon \nabla_{P^*}(\nabla_{P^*} + \beta \nabla_{P^*} H_s)\, W(\mathbf{R}, \mathbf{P}^*, t) \tag{3.23}$$

For time scales of interest for the Brownian system, the integral in Eq. (3.23) can be extended to infinity and all we need to know is $\int_0^\infty d\sigma\, \mathsf{C}(\mathbf{R}, \sigma)$.

Finally, the initial value term in Eq. (2.16) decays to zero for times greater than τ_b and we obtain the usual Fokker–Planck equation. Under these circumstances, averages of the Langevin equation can be taken over the distribution function $\tilde{\rho}$ and the average fluctuating force is zero.

3.3. Harmonic Oscillator Systems(8)

We have already seen that terms of the form $e^{-L_s \sigma} \nabla_P \mathbf{P}_0(\sigma)$ simplify dramatically when the system Hamiltonian is that for a harmonic oscillator; see Eq. (3.11). Indeed, the generalized Langevin and Fokker–Planck equations simplify dramatically when the system and bath are both harmonic and the coupling between them is bilinear. We note that if the interaction is not of this form, serious difficulties can occur.

The Hamiltonian for this overall system is given by Eq. (2.1) with

$$H_s = P^2/2M + 1/2M\Omega^2 R^2 \tag{3.24a}$$

$$H_b = \sum_{j=1}^{N} (p_j^2/2m + 1/2m\omega_j^2 r_j^2) \tag{3.24b}$$

and

$$H_I = -\sum_j \lambda_j r_j R \tag{3.24c}$$

For proper behavior of this interaction, the coupling constant λ_j must be of order $N^{-1/2}$.

It is convenient to introduce the variable y_j, where

$$y_j \equiv r_j - \frac{\lambda_j R}{m\omega_j^2} \tag{3.25}$$

and to rewrite the Hamiltonian for the overall system as

$$H = P^2/2M + 1/2M\tilde{\Omega}^2 R^2 + \sum_{j=1}^{N} (p_j^2/2m + 1/2m\omega_j^2 y_j^2) \tag{3.26}$$

where

$$\tilde{\Omega}^2 = \Omega^2 - \sum_j \frac{\lambda_j^2}{Mm\omega_j^2} \tag{3.27}$$

The subtractive term in Eq. (3.27) can be eliminated by adding a term $\sum_j(\lambda_j^2/2m\omega_j^2)\,R^2$ to the total Hamiltonian.

The distribution function $\tilde{\rho}$ for this case is given by

$$\tilde{\rho} = \prod_{j=1}^{N} \frac{\exp[-\beta(p_j^2/2m + 1/2m\omega_j^2 y_j^2)]}{\int dy_j\, dp_j \exp[-\beta(p_j^2/2m + 1/2m\omega_j^2 y_j^2)]} \tag{3.28}$$

and the equations of motion are

$$\begin{aligned} \dot{y}_j &= p_j/m - (\lambda_j/mM\omega_j^2)P, & \dot{p}_j &= -m\omega_j^2 y_j \\ \dot{R} &= P/M, & \dot{P} &= -M\tilde{\Omega}^2 R + \sum_j \lambda_j y_j \end{aligned} \tag{3.29}$$

Equation (2.9) becomes

$$\begin{aligned} \dot{G}(t) &= K_G(t) + [(P/M\nabla_R - M\tilde{\Omega}^2 R\nabla_P)G](t) \\ &\quad + \int_0^t d\sigma\, e^{L(t-\sigma)}(\nabla_P - \beta P/M) \sum_{j,j'} \lambda_j\lambda_{j'} \langle y_{j'} e^{(1-P)L\sigma} y_j\rangle \nabla_P G \end{aligned} \tag{3.30}$$

where the average is over $\tilde{\rho}$ and the operator $e^{(1-P)Lt}$ acts on y_j and $\nabla_P G$. Here

$$K_G(t) = e^{(1-P)Lt} \sum_j \lambda_j y_j \nabla_P G \tag{3.31}$$

Note that the fluctuating force $K_G(t)$ is at least multiplicative unless $G = P$.

For $G = P$, the kernel in Eq. (3.30) is simple to evaluate and we obtain

$$\sum_{j,j'} \lambda_j \lambda_{j'} \langle y_{j'} e^{(1-P)Lt} y_j \rangle = \sum_j \lambda_j^2 \langle y_j^2 \rangle \cos \omega_j t = I(t) \tag{3.32}$$

The integral in Eq. (3.30) then becomes

$$\int_0^t d\sigma \, I(\sigma) \frac{-\beta P(t-\sigma)}{M} \tag{3.33}$$

The simplification in Eq. (3.32) does not occur unless $G = P$. For other functions we do not obtain a generalized Langevin equation. Furthermore, we do not obtain a generalized Fokker–Planck equation unless the interaction is weak.

The harmonic oscillator system is special in a variety of ways. The isolated bath has no mechanism for equilibration and this can cause serious difficulties if the interaction term is nonlinear in bath coordinates.(9)

4. APPLICATIONS TO CHEMICAL REACTIONS IN CONDENSED PHASES

In Section 3, we have shown that the exact equations for the time dependence of $G(t)$, Eq. (2.9), and for $W(t)$, Eq. (2.16), reduce to generalized Langevin and Fokker–Planck equations under restrictive conditions which involve weak coupling, Brownian motion, or special Hamiltonians (e.g., harmonic oscillator systems). Even under these restrictions, simple results are obtained only when the interaction potential is of a special form. These special forms include potentials which are linear in the system coordinate or in which the interaction potential depends on the relative distance, $|\mathbf{r} - \mathbf{R}|$. Even more restrictive conditions apply to the interaction potential for harmonic systems. If the interaction term for these systems is quadratic in the bath coordinate, serious difficulties arise because r_j^2 has a projection onto the constants of the motion of the bath.

The application of the results of Section 3 to chemical reactions in condensed phases severely restricts the types of reactions that can be treated. We consider the simplest type of reaction in which there is one reaction coordinate for which the potential is of standard form, i.e., a well with an infinite wall on one side and a finite wall on the other. Reaction occurs when the system goes over the top of the finite barrier.(10)

The overall system consists of one solute molecule which can react and N solvent molecules which mediate the reaction. In this case the bath degrees of freedom include the positions and momenta of the solvent molecules, the center-of-mass position and momentum of the solute molecule, and the rotational motion of the solute molecule. The system degrees of freedom consist of the reaction coordinate and its conjugate momentum. Thus, the bath has $6N+12$ degrees of freedom for spherical solvent molecules and a nonlinear solute molecule and the system has two degrees of freedom, R and P. The motion of the system degrees of freedom takes place in the potential of the isolated solute molecule as modified by the potential of mean force, $w(R)$, due to interaction with the bath degrees of freedom. In the following, we shall discuss the applicability of the various regimes delineated in Section 3 to chemical reactions in condensed phases.

4.1. Weak Coupling

In the weak coupling regime discussed in Section 3, we have assumed that the potential of interaction between the bath and the system ϕ and its spatial derivative $\nabla_R \phi$ are small. Similar results can be obtained for arbitrary ϕ but small $\nabla_R \phi$ and $\nabla_R w$. We can then apply the results of Section 3.1 to the situation in which there is an R-independent change in the potential of the isolated solute molecule. Unfortunately, in many reactions in solution, the potential of mean force is strongly R dependent and the change in the reaction coordinate potential is strongly R dependent. Under these conditions weak coupling cannot be applied and the exact equations do not reduce to a useful form.

4.2. Brownian Motion

If the internal motions of the solute molecule are slow and its momentum is large, we can apply the considerations of Section 3.2 to reactions in solution. This will apply if the well is broad and the classical Kramers treatment will apply.(11) Note that the friction coefficient for this case is small since it contains a factor of m/M. In many cases, if the internal motions are slow, e.g., for the I_2 molecule, the translational and rotational motions of the molecule will also be slow and we will obtain a Fokker–Planck equation for the reduced distribution function of all of the degrees of freedom of the solute molecule.

4.3. Harmonic Oscillator Systems

Many investigators have studied harmonic oscillator systems(12) with bilinear interaction potentials as prototypes for discussing chemical reactions in condensed phases. These studies have utilized the Langevin equation for the momentum or the normal mode properties of the overall system or both. In these studies the bottom of the well is modeled by a harmonic oscillator and the barrier by an inverted harmonic oscillator. It is sometimes useful(6) to use action–angle variables to describe the system, although there are difficulties with this approach near the top of the barrier.

The use of harmonic oscillator systems for the description of chemical reactions in solids is well-founded. However, the application of these ideas to chemical reactions in liquids must be investigated carefully. If the bath is modeled by a collection of noninteracting harmonic oscillators with a dense frequency spectrum from zero to some cutoff frequency, all of the diffusional motions of the bath are suppressed. The diffusion constant for the bath is zero and its thermal conductivity is infinite.

Several investigators have studied the normal mode frequency distribution of a liquid and have found both stable and unstable modes.(13) The unstable modes have imaginary frequencies similar to those found for the inverted harmonic oscillator which has been used to model the shape of the barrier for the reacting system. The nonzero diffusion constant for the bath is due to the finite lifetime of the stable mode oscillations. The unstable mode oscillations have even a shorter lifetime. In the simplest case, then, the sum over frequencies in Eq. (3.32) must include both stable and unstable modes both with finite lifetimes. The study of these effects on chemical reactions in liquids is underway.

5. CONCLUSIONS

We have studied the conditions under which the exact equations for the time dependence of a dynamical variable, Eq. (2.9), and for the time dependence of a reduced distribution function, Eq. (2.16), reduce to generalized Langevin or Fokker–Planck equations. This reduction is justifiable from molecular considerations under the restricted conditions of weak coupling, Brownian motion, or harmonic systems with special types of interaction potentials.

The range of chemical reactions in condensed phase which can be described using these reduced equations is severely limited.

We end with a word of caution. It is frequently found that the useful range of approximations is considerably broader than their justifiable range. The crucial test is whether the results of the theory agree with experiment or computer simulations. The computer simulations must be performed using the exact dynamics and not some approximation to them.

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