I. INTRODUCTION

Chemical reactions in condensed phases are frequently described using two different methods. The simple approach consists of a Brownian particle moving in a one-dimensional bistable potential. In this case, the dynamics of this system can be described by the Langevin equation. Grote and Hynes have extended this approach to non-Markovian processes for a parabolic barrier, where the dynamics are given by the generalized Langevin equation (GLE). These and other theories were tested numerically by Straub, Borkovec, and Berne, and their results were crucial in the development of the Pollak, Grabert, and Hänggi turnover theory.

The other approach, which became more common, is based on molecular dynamics simulations, and can account for a general form of the Hamiltonian. Special methods have been developed to accelerate the barrier crossing and thereby numerically determine the rate constant. Chandler showed that in the time-correlation approach to rate constants, the reactive flux rapidly decays to a plateau value, which can then be associated with the slow rate for crossing the barrier. For cases in which no preconceived notion of mechanism or transition state is known, a more general computational method, called the “transition path sampling,” has recently been developed and applied to complex reactive systems.

One of the major limitations of the simple approach based on the GLE formalism mentioned above is related to how one can evaluate the frequency dependent memory friction (related to the random force by the fluctuation dissipation theorem). Most applications assume a Gaussian random force for the GLE. In this limit, the dynamics can be transformed into a Hamiltonian description where the system is linearly coupled to a harmonic bath. Bagchi and his co-workers have used a mode-coupling theory to generalize this approach in order to include non-Gaussian fluctuations. Their goal was to explain the coexistence of large barrier frequency with not-so-small viscosity exponent. For this purpose, they assumed that the translational friction is the principal quantity that regulates the diffusive Brownian motion of the reactive system near the barrier region. In this limit, the memory friction is simply given by the Sjögren and Sjölander mode-coupling expression for the memory kernel of a GLE for self-motion in neat liquids.

In this paper we develop an alternative theory to treat non-Gaussian fluctuations within the GLE formalism. First, following the work of Oppenheim and his co-workers, we derive a GLE for the dynamics of a reactive system in a liquid host. Based on the formal expression for the memory friction of this GLE, and using a combination of kinetic and mode-coupling theories, we obtain a simple expression for the memory friction. This memory friction is then used to obtain the reaction rate within the framework of the Grote–Hynes theory. Our approach is different from that of Bagchi and co-workers in two ways: First, we need not assume that the translational friction is the principal quantity that regulates the diffusive Brownian motion of the reactive system. Second, it can be shown that this assumption limits the form of the couplings between the system and the liquid host. Thus, a more general form of the Hamiltonian can be treated within our formulation.

Our paper is organized as follows: In Sec. II we provide a derivation of the GLE, an overview of the Grote–Hynes theory, and a derivation of our kinetic and mode-coupling theories. Tests of our approach for a model isomerization reaction in a Lennard-Jones (LJ) fluid are provided in Sec. III. Finally, we conclude in Sec. IV.
A. Generalized Langevin equation

Consider a general Hamiltonian for a reactive system in a liquid host of the form

\[ H = H_s(R,P) + H_b(r,p) + \phi(R,r), \]

where \( H_s(R,P) \) is the Hamiltonian of a reactive one-dimensional system with phase-space coordinates \( R \) and \( P \), and reduced mass \( \mu \), \( H_b(r,p) \) is the Hamiltonian of \( N \) interacting liquid particles with phase-space coordinates \( r \) and \( p \), and mass \( m \), and \( \phi(R,r) \) is the coupling between the system and the solvent.

Using the projection operator formalism of Zwanzig and Mor, we now derive reduced equations of motion for the system. First, we define a projection operator \( P \) that projects out the bath variables,

\[ \mathbb{P} = \int dr dp \rho_b(r,p)B = \langle B \rangle, \]

where

\[ \rho_b(r,p) = \rho_b(r,p) \exp \left( -\beta \left( \phi(R,r) - w(R) \right) \right). \]

In the above equation \( \beta = 1/k_B T \) is the inverse temperature, \( \rho_b(r,p) = \exp \left( -\beta H_b(r,p) \right) / Z_b \) is the equilibrium distribution function for the isolated bath, \( Z_b \) is the partition function of the isolated bath, and \( w(R) \) is the potential of mean force, given by

\[ \exp \left( -\beta w(R) \right) = \int dr dp \rho_b(r,p) \exp \left( -\beta \phi(R,r) \right). \]

Using the above projection operator it is straightforward to show that the reduced equations of motion for the system are given by the GLE form:26

\[ \dot{R} = \frac{P}{\mu} \]

and

\[ \dot{P} = -e^{iLt} \left[ \frac{\partial H_s}{\partial R} - \frac{\partial w}{\partial R} \right] + K(t) \]

\[ \quad - \frac{\beta}{\mu} \int_0^t d\tau e^{iL\tau} \mathbb{P} \langle KK(t-\tau) \rangle, \]

where, as noted above, \( \mu \) is the reduced mass of the system, the \( \langle \cdots \rangle \) is defined in Eq. (2), \( e^{iLt} \) is the classical propagator with \( iL = \{ H_s \cdots \} \), and the random force \( K(t) \) is given by

\[ K(t) = -e^{i(t-\tau)L_t} \frac{\partial}{\partial R} \left( \phi(R,r) - w(R) \right). \]

Note that the random force involves \textit{projected} propagation where the classical propagator \( e^{iLt} \) is replaced by the projected propagator \( e^{i(t-\tau)L_t} \).

The memory kernel of the above GLE is related to the random force by the fluctuation dissipation theorem, and is given by

\[ \zeta(t) = \frac{\beta}{\mu} \langle KK(t) \rangle. \]

This correlation function is, in general, a function of time and a function of the system coordinate \( R \) [cf. Eq. (7)].

B. Grote–Hynes theory

To obtain the reaction rate one needs to solve the GLE given by Eq. (6). However, as a result of the fact that the random force involves projected propagation of the couplings between the system and the bath, a complete solution of this GLE is an extremely difficult task. To circumvent this problem, Grote and Hynes have developed an approximate theory to obtain the rate within the GLE formulation.27

The basic assumption made by Grote and Hynes is that in the \textit{barrier region}, the dynamics can also be described by the above GLE, where the deterministic force (given by \( [\partial H_s / \partial R] - (\partial w / \partial R) \)) is replaced with an inverse parabolic approximation. After some lengthy algebra, Grote and Hynes obtained the following simple expression for the transmission coefficient \( \kappa \):

\[ \kappa = \frac{k}{k_{TST}} = \frac{\lambda_r}{\omega_b}, \]

where \( \lambda_r = \omega_b^2 / (\lambda_r + \tilde{\xi}^\dagger(\lambda_r)) \) is the Laplace transform of \( \tilde{\xi}^\dagger(\lambda_r) \) given by

\[ \tilde{\xi}^\dagger(\lambda_r) = \int_0^\infty dt e^{-\lambda_r t} \tilde{\xi}(t), \]

and the symbol ‘‘\dagger’’ indicates that the observable is evaluated at the saddle point, namely, in the barrier region as required by the Grote–Hynes theory. To obtain the rate, Eq. (10) must be solved self-consistently.

The Grote–Hynes expression for the rate reduces to Kramer’s result if the memory friction decays rapidly on time scales faster than the system’s motion.3 In the strong friction limit, \( \tilde{\xi}^\dagger(\lambda_r) / \mu \gg \lambda_r \), the reactive frequency will be much smaller than the barrier frequency resulting in a small transmission coefficient. In the weak friction limit, \( \tilde{\xi}^\dagger(\lambda_r) / \mu \ll \lambda_r \), the reactive frequency simply equals the barrier frequency \( (\lambda_r = \omega_b) \), and the rate is given by the transition state rate. This is a shortcoming of the approximation made by Grote and Hynes which fails to capture the turn over to Kramer’s spatial diffusion regime. Hence, the above Grote–Hynes rate expression is valid only for high frictions.

The approach developed by Grote and Hynes reduces the complexity of solving the GLE to that of estimating the memory friction of the GLE. For such problems, a very powerful approach has been developed and applied to many interesting dynamical problems in solutions. In the following subsection we describe a combination of kinetic and mode-coupling theories that we have developed to model the memory friction of the GLE in order to study reaction dynamics in liquids.
C. Kinetic and mode-coupling theories

One major difficulty in evaluating the memory kernel of the GLE given in Eq. (6) is that the correlation of the random force involves propagation of \( \phi(R, r) - w(R) \) in the projected subspace spanned by \( Q = 1 - P \) [see Eq. (7)]. To overcome this difficulty we develop a theory to calculate \( \xi(t) \) that is based on a combination of kinetic and mode-coupling theories.\(^{19}\) This combination has been used to study density and current fluctuations,\(^{19–21}\) solvation and relaxation dynamics,\(^{23,31,32}\) and nonlinear spectroscopy\(^{33–35}\) in classical liquids. A quantum mechanical generalization of this approach has recently been developed and applied successfully to study the dynamic response in quantum liquids.\(^{36–42}\)

The Grote–Hynes approach requires that the memory friction be approximated in the barrier region. We therefore replace the full memory friction of the GLE (\( \xi(t) \)) with that approximated at the saddle point (\( \hat{\xi}(t) \)), where (as before) the symbol “\( \hat{\cdot} \)” indicates that the position variable of the system is taken at the saddle point. Next, we replace \( \hat{\xi}(t) \) with an approximate form given by\(^{43}\)

\[
\hat{\xi}(t) = \hat{\xi}_b(t) + \hat{\xi}_{MC}(t),
\]

where \( \hat{\xi}_b(t) \) and \( \hat{\xi}_{MC}(t) \) are the “binary” and “mode-coupling” terms of the memory friction, respectively. The fast decaying binary term is determined from a short-time expansion (to second order in time) of the exact memory friction, and is given by

\[
\hat{\xi}_b(t) = \hat{\xi}(0) \exp(- (t/\tau)^2),
\]

where the lifetime \( \tau \) is given by

\[
\frac{1}{\tau} = -\frac{1}{2} \frac{\partial^2}{\partial q^2} \hat{\xi}(0).
\]

In the above equations \( \hat{\xi}(0) \) and \( \hat{\xi}(0) \) are the zero and second time moments of the memory friction, and are given by

\[
\hat{\xi}(0) = \frac{\beta}{\mu} \left\{ \left[ \frac{\partial}{\partial R^i} (\phi(R^i, r) - w(R^i)) \right]^2 \right\},
\]

and

\[
\hat{\xi}(0) = -\frac{1}{m \mu} \left\{ \left[ \frac{\partial}{\partial R^i} \frac{\partial}{\partial R^j} (\phi(R^j, r) - w(R^i)) \right]^2 \right\}.
\]

As noted above, \( \mu \) is the reduced mass of the system, and \( m \) is the mass of a liquid particle.

The slow decaying mode-coupling portion of the memory kernel, \( \hat{\xi}_{MC}(t) \), must be obtained from a mode-coupling approach. The basic idea behind this approach is that the random force projected correlation function decays at intermediate and long times predominantly into modes that are associated with quasiconserved dynamical variables. It is reasonable to assume that the decay of the memory kernel at long times will be governed by those modes that have the longest relaxation time. In the present application the slow decay is basically attributed to couplings between wave-vector-dependent density modes of the form

\[ b_{k,q} = e^{i k \cdot r_j} n_q, \]

where the self-density mode is given by

\[ c_k = e^{i k \cdot r_j}, \]

with \( r_j \) being the coordinate of liquid particle \( j \), and the density mode is given by

\[ n_k = \sum_{q=1}^{N} e^{i k \cdot r_j}, \]

for \( N \) liquid particles. We note that it is possible to include other modes, such as longitudinal and transverse current modes.\(^{19}\) However, for the specific application discussed below, we find that including only the above density modes is sufficient to obtain quantitative results.

In practice, the simplest way to extract the dominant slow contribution of the decay of the memory friction is to introduce another projection operator, \( P_2 \) given by

\[
P_2 = \sum_{q=1}^{N} \frac{b_{k,q}}{\eta S(q)} (b_{k,-q},...,),
\]

that projects any variables on the space spanned by the slow modes \( c_k \) and \( n_q \). Then, following the common approximations in which the projected dynamics of the random force is replaced with the dynamics projected onto these slow variables, and replacing four-point density correlations with a product of two-point density correlations,\(^{19–21}\) we find that \( \hat{\xi}_{MC}(t) \) is given by

\[
\hat{\xi}_{MC}(t) = \frac{\beta}{\mu \rho} \int \frac{d^3q}{(2\pi)^3} \left[ \left| V(q) \right|^2/S(q)^2 \right] 
\times \left[ F_s(q,t) F(q,t) - F_{sb}(q,t) F_{sb}(q,t) \right].
\]

In the above equation \( \rho \) is the liquid number density, \( S(q) \) is the structure factor of the neat fluid, \( F_s(q,t) \) and \( F(q,t) \) are the self-intermediate and intermediate scattering functions of the neat fluid, respectively, and the vertex is given by the static average of the product of the coupling force and the slow modes,

\[
V(q) = \left\{ \frac{\partial}{\partial R^i} [\phi(R^i, r) - w(R^i)] b_{q,-q} \right\}.
\]

As before, the symbol “\( \hat{\cdot} \)” indicates that the coupling force is evaluated at the saddle point.

The binary self-intermediate and binary intermediate scattering functions are given by

\[
F_{sb}(q,t) = \exp \left\{ -\frac{q^2 \tau^2}{2\beta m} \right\}
\]

and

\[
F_s(q,t) = S(q) \exp \left\{ -\frac{q^2 \tau^2}{2\beta m S(q)} \right\}.
\]

The subtraction of the product of these terms in Eq. (21) is done to prevent over counting the total memory kernel at short times, namely, to ensure that the even time moments of the total memory kernel are exact to fourth order in time.

To obtain the memory friction one requires as input the first two moments \( \hat{\xi}(0) \) and \( \hat{\xi}(0) \), the static structure factor \( S(q) \), and the vertex \( V(q) \). These static averages...
can be obtained from simulations, or from the proper integral equation formulation. In addition, we need the self-intermediate and intermediate scattering functions. These time-dependent correlation functions of the neat fluid can be obtained from simulations, or alternatively from a similar mode-coupling approach, where a GLE for the density fluctuations is solved using a combination of kinetic and mode-coupling theories.19–21

III. RESULTS

To assess the accuracy of the proposed theory we have studied the rate of a model for an isomerization reaction of a diatomic molecule in a Lennard-Jones (LJ) fluid. The Hamiltonian of the entire system and bath can be described by Eq. (1). The isomerizing diatomic molecule is made of two atoms with equal mass \( m^* \), interacting via a symmetric double-well potential. Without loss of generality, we place the atoms along the \( z \) axis, where the position vectors are \( R_1 = (0,0,0) \) and \( R_2 = (0,0,R) \) for atom 1 and 2, respectively. The reaction coordinate is taken as the distance \( R = |R_1 - R_2| \) separating the atoms. We allow the atoms to move only along the \( z \) axis (which is the reaction coordinate). The reactive system Hamiltonian can be described by

\[
H(R, P) = \frac{p^2}{2\mu} + V_0\left\{4[(R - R^*)/\alpha]^2 - 1\right\}^2, \tag{25}
\]

where \( \mu = m^*/2 \) is the reduced mass of the system, \( V_0 \) is energy barrier separating reactants from products, \( R^* \) is the location of the transition state, and \( \alpha \) is the distance between the two minima corresponding to stable reactants and products. For the results shown below we take \( R^* = 2.16^\circ \alpha \), \( V_0 = 5k_BT \), \( T = 2.5e \), \( \alpha = 2\sigma/3 \), and a reduced mass \( \mu = 1/2 \) for the isomerizing diatomic molecule.

The solvent Hamiltonian is given by the LJ form,

\[
H_s(r,p) = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{i>j=1}^{N} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]. \tag{26}
\]

where \( r_j \) is the position vector of liquid particle \( j \) with momentum \( p_j \) and mass \( m \), and \( r_{ij} = |r_j - r_i| \).

For simplicity we take the solute–solvent interaction to be a two-site LJ potential in which each site of the molecule interacts with the solvent atoms through precisely the same LJ potential,

\[
\phi(R, r) = \sum_{j=1}^{N} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{j=1}^{N} 4\epsilon \left[ \left( \frac{\sigma}{r_{2j}} \right)^{12} - \left( \frac{\sigma}{r_{2j}} \right)^6 \right]. \tag{27}
\]

Here \( r_{ij} = |r_j - R_1| \). In the application of the mode-coupling theory we need to evaluate the derivative of \( \phi(R, r) \) with respect to the reaction coordinate \( R \). This is done using the chain rule, and the result is given by

\[
\frac{\partial \phi(R, r)}{\partial R} = \frac{1}{2} \left( \frac{\partial \phi(R, r)}{\partial Z_2} - \frac{\partial \phi(R, r)}{\partial Z_1} \right), \tag{28}
\]

where \( Z_1 \) and \( Z_2 \) are the \( z \) components of the position vector of the diatomic molecule \( R_1 \) and \( R_2 \), respectively, and the factor \( 1/2 \) comes from the Jacobian. The derivatives of \( \phi(R, r) \) along the other directions vanish since the system is frozen along the \( z \) axis.

To test our approach, we have calculated the static and dynamic input required to obtain the time-dependent friction, using the molecular dynamics (MD) simulation techniques. While other approaches, such as the integral equation theory and a proper mode-coupling treatment of density fluctuations, can be used to obtain the static and dynamic input, we feel that a fare test of our theory should rely on numerically exact input. Thus, despite the success of the theoretical approach in predicting structural44 and dynamical45 properties in LJ systems, we limit our study to the more accurate simulation approach.

The static input was obtained using the MD method for \( N = 500 \) particles (including the diatomic) and for a set of densities \( \rho = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 \) in reduced LJ units.46 Approximately \( 10^6 \) MD steps were made for each density. Every 50 steps we collected data for \( \xi^1(0), \xi^2(0), S(q) \) and for the vertex \( V(q) \). The self-intermediate and intermediate scattering functions were also calculated using the MD method for identical conditions. The results for each density were averaged over 10 different runs of total run time of \( t = 15 \) reduced LJ units.

In Fig. 1 we plot the direct correlation function, \( c(q) = (S(q) - 1)/\rho S(q) \), and the vertex squared for all densities studied in this work. The features observed for the direct correlation function are well understood, and have been discussed elsewhere.21 The magnitude of the vertex given by \( V(q) = (\partial^2/\partial R^2) [\phi(R, r) - w(R)] \delta_{q,q} \) determines the contribution of the different density modes to the decay of the memory friction at intermediate and long times. We find that at high liquid densities the major contribution comes from modes with a characteristic wavelength of \( q \approx 2\pi/\alpha \). This wavelength corresponds to the average interparticle separation, and its value slightly increases with decreasing density.
density [note the shift in the position of the first maximum of $c(q)$ with density]. Thus, density modes associated with liquid motion on length scales of the interparticle separation (namely, on length scale of $\sigma$) contribute the most to the friction at intermediate and long times.

As expected, the contribution of lower wavelengths to the decay of the memory friction becomes more significant at lower liquid densities. In fact, at the lowest density studied, the contribution of density modes below $q \approx 2\pi/\sigma$ to the decay of the memory friction at intermediate and long times is more significant than the contribution of modes near the first peak in $c(q)$. We attribute this effect to the change in the mechanism of self-diffusion of liquid particles. At high liquid densities, the self-diffusion is dominated by opening of the cage surrounding a system, with a typical length scale of $\sigma$ related to the size of the cage. This is not true at low liquid densities, where liquid particles can hop over much larger distances. In addition, we find that motion within the cage becomes significant at higher liquid densities, as reflected in nonvanishing values of the vertex above $q \approx 2\pi/\sigma$.

Using the static input along with the self-intermediate and intermediate scattering functions obtained from MD simulations, we have calculated the total memory friction given by Eqs. (13) and (21). The results are shown in Fig. 2 for all densities studied in this work. As can be seen, the decay of the memory friction is characterized by two time scales. A fast decay given by $\tilde{\zeta}_B(t)$ followed by a slower decay given by $\tilde{\zeta}_{MC}(t)$. The contribution of the mode-coupling portion to the total memory friction is significant only at high liquid densities. At the lower densities studied the mode-coupling portion of the memory friction is negligible.

For the specific model studied here where the solute–solvent interactions are equal to the solvent–solvent interactions, the memory friction can also be obtained by inverting the GLE for the velocity autocorrelation function of a neat fluid. Straub, Borkovec, and Berne have calculated the velocity autocorrelation function for the LJ fluid using the MD technique, and obtained the memory friction by inverting the proper GLE. Our results obtained from the mode-coupling theory agree well with their simulated results (not shown). Specifically, we find that the decay of the memory friction at short times is nearly independent on the liquid density, in agreement with the simulation results. Moreover, at high liquid densities, our theory provides semiquantitative agreement with the molecular dynamics results at all times. For low liquid densities, we observe small deviations from the simulation results at intermediate times. This shortcoming of the mode-coupling approach is expected since the simulated memory friction becomes slightly negative at intermediate times, and the mode-coupling approximation is known to fail under such circumstances. However, since the contribution of the mode-coupling portion to the memory friction is relatively small at these low densities, this has a vanishing effect on the value of the transmission coefficient.

Using the memory friction obtained from the kinetic and mode-coupling theory we have calculated the transmission coefficient by solving Eqs. (9) and (10) self-consistently. The results for $\kappa$ as a function of the integrated friction $\tilde{\zeta}^1(0)$ [cf. Eq. (11)] are shown in Fig. 3. We compare our results to the results obtained by the weak collision theory (based on a simple connection formula) using an exponential friction, and to Kramer’s theory. For the present model the weak collision theory provides a quantitative agreement for the transmission coefficient (within the noise level of the simulations) in comparison with results obtained using the absorbing boundary approximation to the reactive-flux formalism. As can be seen, our theory provides quantitative results for the transmission coefficient over the entire range of frictions studied.

The different values of the integrated friction $\tilde{\zeta}^1(0)$ at
which we have calculated $\kappa$ were obtained by scanning the liquid density from low $\rho = 0.5$ to high $\rho = 1.0$ values. For each density we have calculated the static and dynamic input required by our mode-coupling theory, and obtained the transmission coefficient by solving Eq. (9) self-consistently. Alternatively, one can control the integrated friction $\hat{\xi}(0)$ by changing the value of the reduced mass $\mu$ of the isomerizing diatomic molecule [cf. Eq. (8)]. We find that our mode-coupling theory provides similar quantitative results (not shown) for the transmission coefficient when the reduced mass of the isomerizing diatomic molecule is varied.

IV. CONCLUSIONS

We have presented a theoretical approach for the calculation of reaction rates in condensed phases based on the Grote–Hynes formalism. A combination of kinetic and mode-coupling theories were developed to obtain the memory friction required by the Grote–Hynes theory. The approach was applied to study a model isomerization reaction of a diatomic molecule in a LJ fluid. Good agreement for the transmission coefficient was obtained in comparison with the simulation results of Straub, Borkovec, and Berne\(^8\) based on the reactive flux formalism.

Unlike simulation techniques, our approach is a theory and thus provides additional insight into the reaction dynamics in liquids. For example, we showed that the contribution of the mode-coupling portion to the decay of the memory kernel at intermediate times is significant only at high liquid densities. Thus, an accurate description of the reaction dynamics at low liquid densities can be obtained from a kinetic theory alone. Furthermore, the mechanism for the decay of the memory friction (which is reflected in the reaction rate) is quite different at low versus high liquid densities. At high liquid densities the decay of $\hat{\xi}(t)$ is dominated by liquid modes with a long scale compared to the separation between the fluid particles, while at lower liquid densities motion on larger length scales also contributes the decay of $\hat{\xi}(t)$. This is significant for the development of coarse grained models for reaction dynamics.

We believe that our approach will be useful in other situations in which simulation techniques are still limited. For example, for reaction dynamics in supercooled liquids that are characterized by slow density fluctuations. Or for liquid hosts that are characterized by quantum mechanical susceptibilities. Work along these directions is currently underway.

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