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Generalized Langevin theory for many-body problems in chemical dynamics: The equivalent chain equations for solute motion in molecular solvents

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A generalized Langevin equation framework for the treatment of liquid state influence on solute dynamics in molecular solvents, which generalizes an earlier framework restricted to monatomic solvents [S. A. Adelman, Adv. Chem. Phys. **53**, 61 (1983)], is developed. This framework permits one to realistically treat energy exchange between the solute atoms and the solvent vibrational (V) degrees of freedom. This energy exchange can qualitatively influence the rates of liquid state processes when the solute frequencies relevant to the process of interest (e.g., a solute normal mode frequency if one is interested in the vibrational energy relaxation of that mode) substantially overlap the V bands of the frequency spectrum describing local solvent density fluctuations. The main result of the present analysis is an infinite set of equivalent chain equations governing the dynamics of the solute configuration point in molecular solvents. These are equations of motion for the solute configuration point and for the coordinates of an infinite set of abstract chain "molecules". Each molecule is composed of $r + 1$ "atoms" where r is the number of normal modes of a real solvent molecule. The nearest neighbor chain of fictitious molecules may alternatively be regarded as a set of $r + 1$ nearest neighbor cross-linked "atomic" chains. Atomic chain 1 executes low frequency "acoustical" motions which simulate the influence of local solvent translational–rotational (TR) density fluctuations. Atomic chains 2,3,...,$r + 1$ execute high frequency "optical" motions which simulate the influence of normal mode V local solvent density fluctuations. The coupling of the optical and acoustical branches of the chain by the crosslinks is the chain formalism equivalent of the physical coupling, due to liquid state effects, of the temporal development of the TR and V modes of motion. The theory presented in this paper provides a conceptual foundation for the treatment of liquid state reactions occurring in molecular solvents by stochastic dynamics techniques. This conceptual foundation may be made the basis of practical simulation methods for treating reactions of diatomic solutes in molecular solvents and may be further developed to provide practical simulation methods for polyatomic solutes in molecular solvents.

I. INTRODUCTION

Recently we have developed[1] and applied[2] a conceptual framework for the molecular level treatment of problems in condensed phase chemical kinetics by generalized Langevin equation or stochastic dynamics techniques. This framework, which we call the MTGLE[1] theory, is based on the modern time correlation function approach to Brownian motion and irreversible dynamics due to Mori,[3] Kubo,[4] and Zwanzig.[5]

The conceptual framework has been developed into a detailed calculation methodology[1] for the prototype problem of solute motion in monatomic solvents. This paper is the first in a two-part series which will generalize the monatomic solvent theory to provide a stochastic dynamics framework for solute motion in the molecular solvents of actual interest in chemistry. Application of this new theory to specific chemical processes occuring in molecular solvents are planned for future papers.

To motivate the present generalization it is necessary to briefly discuss some aspects of the physical nature of the monatomic solvent effect on solute motion. These aspects emerged from recent stochastic dynamics studies[2] of prototype condensed phase chemical processes.

These prototype studies have established the basic role played by dynamic[6] solvent effects in liquid state chemical kinetics. It is these dynamic solvent effects which render liquid state and gas phase reagent motions qualitatively different.

The dynamic solvent effects may be decomposed into instantaneous and delayed components.[1] The instantaneous component arises from restoring forces exerted on the solute *immediately after* it moves from configuration point r_0 to a neighboring point r_0'. These restoring forces are exerted by the equilibrium local solvent density $\rho(r_0)$ characteristic of the initial configuration point r_0. The delayed component arises from local density relaxation $\rho(r_0) \to \rho(r_0')$ in response to the displacement $r_0 \to r_0'$.

The instantaneous component controls the strong cage confinement forces exerted by the solvent on the solute. The delayed component controls the efficiency of solute–solvent energy exchange processes. It is the interplay between the instantaneous and delayed components, or equivalently between cage effects and energy exchange effects, which give reagent motion in liquids its unique qualitative character.[1,2]

The instantaneous component, for example, provides the molecular basis of the Franck–Rabinowitch caging mod-

el[7] for liquid state photolysis quantum yields. The delayed component introduces new qualitative features, like slow vibrational relaxation,[8] into the dynamics of nascent product thermalization. A subtle competition[2(c)] between instantaneous and delayed components underlies the breakdown of the Kramers[9] picture of condensed phase activated barrier crossing.[10]

We next turn to the new features of liquid state dynamics which must be introduced in order to obtain a realistic picture of solute motion in molecular solvents. The essential character of static and instantaneous dynamic solvent effects is similar in monatomic and molecular solvents. The character of the delayed dynamic solvent effect is, however, qualitatively modified by the vibrational motions of the solvent.[11,12]

The delayed dynamic solvent effects may be quantitatively characterized by dissipation functions $\sigma_1[\omega{:}r_0]$ defined elsewhere.[1] These are the spectral densities of time correlation functions which describe the influence of local temporal solvent density fluctuations on solute motion.

For monatomic solvents the dissipation function has only a low frequency "acoustical" branch. This characterizes the influence of the local translation motions of the solvent atoms. For molecular solvents (composed of molecules each with r normal modes), the dissipation function also has an acoustical branch. This now, however, characterizes the influence of local rotational as well as local translational solvent motions. The dissipation function, moreover, also has r high frequency "optical" branches. These reflect the collective[11] vibrational contribution to the local density fluctuation spectrum.

The central point, as also emphasized by others particularly Nesbitt and Hynes[8] and Wilson and co-workers,[12] is that energy exchange between the solute system and the solvent vibrational motions can qualitatively modify liquid state chemical rates. The effect is most pronounced when such energy exchange is resonant. This occurs when the solute frequencies (e.g., a normal mode frequency) relevant to the process of interest significantly overlap the optical branches of the dissipation function.

This paper is concerned with the development of equations of Brownian motion for the dynamics of the solute configuration point r_0 in molecular solvents. These equations, schematized in Fig. 1, describe cage effects and also energy exchange effects with both solvent translational–rotational (TR) and solvent vibrational (V) degrees of freedom in a physically realistic and calculationally useful manner.

A sequel to the present work will develop the corresponding equations of motion for a small set of chemically relevant explicit solute generalized coordinates x_0. As discussed elsewhere[13] and in Sec. IV, following only explicit coordinate dynamics can lead to significant simplifications.

The outline of this paper is as follows. The idea behind the development and the main results are described in Sec. II. A generalized Langevin equation of motion which decomposes dynamic solvent effects into TR and V contributions is developed in Sec. III. The results presented in Sec. II are developed from this generalized Langevin equation in

the Appendix. Finally we close the paper in Sec. IV with a summary and discussion.

II. BASIC RESULTS

In this section we present the generalized Langevin equations of motion governing the dynamics of the solute configuration point in molecular solvents. We also describe the main ideas behind the development. To motivate the new equations of motion, we first summarize some aspects of the corresponding equations for monatomic solvents.

A. Motivation for separation of acoustical and optical fluctuations

The generalized Langevin equations for monatomic solvents take the form of the infinite set of equivalent chain equations schematized in Fig. 1(a). The motion of chain "atom" 0 simulates the dynamics of the solute configuration point. The motion of chain atoms 1,2,... simulate the influence of local temporal solvent density fluctuations on solute dynamics.

The infinite set may be truncated to yield effective few-body stochastic models which are the basis of the trajectory simulations[2] mentioned in the Introduction. The central point from the present perspective is that a $(p + 1)$-atom truncation amounts to replacing the exact dissipation function $\sigma_1[\omega{;}r_0]$ by a model which precisely reproduces its first $2(p - 1)$ even moments. For monatomic solvents, however,
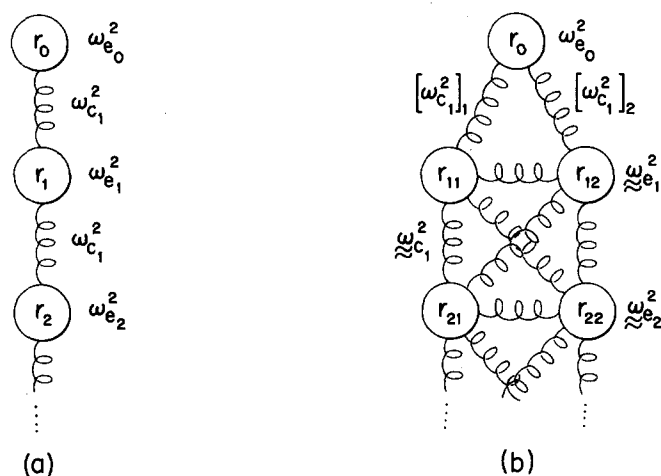

FIG. 1. (a) Equivalent chain equations for solute motion in monatomic solvents. The motion of chain atom 0 simulates the temporal development of the solute configuration point. The motion of chain atoms 1, 2,... simulates the influence of local translational density fluctuations on solute dynamics. Chain atom 1, qualitatively speaking, simulates nearest neighbor contributions, chain atom 2 second nearest neighbor contributions, etc. (b) Equivalent chain equations for solute motion in diatomic solvents. The motion of chain atom 0 simulates the temporal development of the solute configuration point. The motion of chain atoms 11,21,... simulates the influence of local translational–rotational (TR) density fluctuations on solute dynamics. The motion of chain atoms 12,22,... simulates the influence of local vibrational (V) density fluctuations on solute dynamics. Atoms 11 and 12, qualitatively speaking, simulate nearest neighbor contributions, atoms 21 and 22 second nearest neighbor contributions, etc. Crosslinks symbolize the liquid state coupling of the temporal development of the TR and V density fluctuations.

the chemically relevant information in $\sigma_1[\omega;r_0]$ is mainly carried by its first few moments.[1] The lowest order moments, moreover, are equilibrium properties of the liquid solution which may be approximately constructed from solute–solvent pair correlation functions. Consequently short-chain models of the type depicted in Fig. 1(a) provide a realistic and convenient representation of solvent effects in monatomic liquids.[1]

For molecular liquids, the situation is more complex. The low order moments of the dissipation function are often dominated by its acoustical branch. Thus high order moments are required in order to realistically simulate the influence of both the acoustical and the r optical branches. Such high order moments are both difficult to compute and have little physical meaning. A consequence is that long chain models of the type depicted in Fig. 1(a) (we estimate $p = 50$–100 for common solvents like water) are required to realistically simulate solute–solvent energy exchange processes in molecular liquids. Such long chain models are neither conceptually nor calculationally useful.

The above discussion, however, suggests a rough strategy for the development of useful stochastic models for reactions in molecular solvents. Instead of constructing the dynamic solvent response from the single set of full moments of $\sigma_1[\omega;r_0]$, one may instead construct it from $r + 1$ sets of partial moments. The first set of partial moments are integrals over only the acoustical branch of $\sigma_1[\omega;r_0]$, the second set over only the first optical branch of $\sigma_1[\omega;r_0]$, etc.

The main point is that the chemically relevant information in $\sigma_1[\omega;r_0]$ for molecular liquids is contained in its low order partial moments. The lowest order partial moments, moreover, are readily calculable equilibrium properties of the liquid solution. This observation suggests that a construction of useful stochastic models for molecular solvents may be based on the partial moments. This is, in fact, done in Sec. III and the Appendix using a refined version of the partial moment concept. We next present the results.

B. The equivalent chain equations for molecular solvents

The generalized Langevin equations for molecular solvents take the form of the infinite set of equivalent chain equations schematized in Fig. 1(b). The motion of chain atom 0 again simulates the dynamics of the solute configuration point r_0. The influence of local solvent density fluctuations is now, however, simulated by the motion of an infinite set of abstract chain molecules 1,2,.... This nearest neighbor of molecules may alternatively be regarded as a set of $r + 1$ nearest neighbor crosslinked atomic chains. Atomic chain 1 executes low frequency acoustical motions which simulate the influence of local TR density fluctuations. Atomic chains, 2,3,...,$r + 1$ execute high frequency optical motion which simulate the influence of the local solvent V density fluctuations. The crosslinking is the chain formalism equivalent of the physical coupling of the temporal development of all $r + 1$ modes of solvent motion. This coupling will occur because of liquid state effects even if the gas phase couplings due to Coriolis forces, anharmonicities, etc. are negligible. The results for an n-atom solute system written in

the supermatrix notation introduced in Sec. III are (here and below T denotes a matrix transpose)

$$m^{1/2}\ddot{r}_0(t)m^{1/2} = \langle F_{r_0}\rangle_{r_0}(t) - m^{1/2}\omega_{e_0}^2[r_0(t)]m^{1/2}r_0(t)$$
$$+ m^{1/2}\omega_{c_1}^2[r_0(t)]m^{1/2}r_1(t),$$

$$m^{1/2}\ddot{r}_1(t)m^{1/2} = - m^{1/2}\omega_{e_1}^2[r_0(t)]m^{1/2}r_1(t)$$
$$+ m^{1/2}\{\omega_{c_1}^2[r_0(t)]\}^T m^{1/2}r_0(t)$$
$$+ m^{1/2}\omega_{c_2}^2[r_0(t)]m^{1/2}r_2(t),$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$m^{1/2}\ddot{r}_p(t)m^{1/2} = - m^{1/2}\omega_{e_p}^2[r_0(t)]m^{1/2}r_p(t)$$
$$+ m^{1/2}\{\omega_{c_p}^2[r_0(t)]\}^T m^{1/2}r_{p-1}(t)$$
$$+ m^{1/2}\omega_{c_{p+1}}^2[r_0(t)]m^{1/2}r_{p+1}(t),$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$(2.1)$$

where m is the solute mass matrix specified in Ref. 14. The quantities governing solvent forces exerted on the solute are defined in detail in Sec. III and the Appendix. Briefly stated: $\langle F_{r_0}\rangle$ is the mean force [Eq. (3.7)]; $\omega_{e_0}^2(r_0)$ is a force constant (per unit mass) [Eq. (3.9a)] which determines the strength of the instantaneous cage restoring forces; $\omega_{c_1}^2(r_0)$ is an $(r + 1)$-dimensional supervector [Eq. (3.19b)] whose elements govern the strength of coupling of the solute dynamics to the $r + 1$ individual modes of solvent motion; $\omega_{e_p}^2(r_0)$ and $\omega_{c_{p+1}}^2(r_0)$ are $(r + 1)\times(r + 1)$-dimensional supervector force constants [Eq. (A5)] which have rough physical interpretations analogous to those of the corresponding quantities for monatomic solvents[1]; $r_1(t)$, $r_2(t)$,... are $(r + 1)$-dimensional supervector coordinate variables [Eq. (A11)] whose components [see, e.g., Fig. 1(b)] simulate the influence of temporal solvent density fluctuations arising from the $r + 1$ individual TR and V modes of solvent motion.

The equivalent chain equations for molecular solvents may be truncated in a manner analogous to that described elsewhere for monatomic solvents.[1,2] A p-molecule truncation of Eqs. (2.1) yields the following effective few-body stochastic models for solute motion in molecular solvents:

$$m^{1/2}\ddot{r}_0(t)m^{1/2} = \langle F_{r_0}\rangle_{r_0(t)} - m^{1/2}\omega_{e_0}^2[r_0(t)]m^{1/2}r_0(t)$$
$$+ m^{1/2}\omega_{c_1}^2[r_0(t)]m^{1/2}r(t),$$

$$m^{1/2}\ddot{r}_1(t)m^{1/2} = - m^{1/2}\omega_{e_1}^2[r_0(t)]m^{1/2}r_1(t)$$
$$+ m^{1/2}[\omega_{c_1}^2(r_0)]^T m^{1/2}r_0(t)$$
$$+ m^{1/2}\omega_{c_2}^2[r_0(t)]m^{1/2}r_2(t),$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$m^{1/2}\ddot{r}_p(t)m^{1/2} = - m^{1/2}\Omega_p^2[r_0(t)]m^{1/2}r_p(t) + m^{1/2}$$
$$\times [\omega_{c_p}^2[r_0(t)]]^T m^{1/2}r_{p-1}(t)$$
$$- m^{1/2}\beta_{p+1}[r_0(t)]m^{1/2}\dot{r}_p(t)$$
$$+ f_{p+1}[t;r_0(t)], \qquad (2.2a)$$

where the truncation parameters $\Omega_p^2(r_0)$ and β_{p+1} are chosen via Eqs. (A7) and (A8).

The supervector white noise Gaussian random force $\mathbf{f}_{p+1}[t;r_0]$ is statistically determined (cf. Refs. 1 and 2) from $\beta_{p+1}(r_0)$ via the following fluctuation–dissipation relationship:

$$m^{1/2}\langle \mathbf{f}_{p+1}(t+\tau)\mathbf{f}_{p+1}^T(\tau)\rangle_{r_0} m^{-1/2}$$

$$= 2 k_B T \beta_{p+1}[r_0]\delta(t). \tag{2.2b}$$

The main point is that a low order truncation (e.g., $p = 1$ or 2) of Eq. (2.2a) describes solute energy exchange with all $r + 1$ modes of solvent motion in a qualitatively realistic manner. The convergence of the effective few-body models, Eqs. (2.2), with increasing p may, moreover, be systematically tested. The procedures parallel those presented elsewhere for monatomic solvents.[1] We will, therefore, defer this description to later papers where they will be presented in connection with concrete applications.

III. SEPARATION OF ACOUSTICAL AND OPTICAL FLUCTUATIONS IN THE GENERALIZED LANGEVIN EQUATION

We next derive the generalized Langevin equation, Eq. (3.23), which is the starting point for the development of the results of Sec. II. We begin with a specification of the liquid solution.

A. The liquid solution

We assume a one-component polyatomic solvent composed of N_s molecules confined to a volume V. Each molecule is composed of n_s atoms. Immersed in the solvent at infinite dilution is the n-atom solute system. The thermodynamic state of the liquid solution is characterized by its Kelvin temperature T and by its number density $\rho = V^{-1}N_s$.

B. Generalized coordinate description of the solvent

To facilitate the separation of acoustical and optical contributions to the dynamic solvent response, we will utilize the generalized coordinate description of the solvent in Ref. 11.

Specifically, in the notation of Ref. 11, we will specify the configuration point of solvent molecule λ by the $3n_s$ generalized coordinates v_λ and w_λ. The set v_λ are the $r = 3n_s - 6(5)$ normal mode V coordinates of solvent molecule λ. The set w_λ are its $s = 6(5)$ TR coordinates (these, for example, can be the center of mass translational and Euler angle rotational coordinates). The corresponding conjugate generalized momenta will be denoted by p_{v_λ} and p_{w_λ}.

We will correspondingly denote the *full set* of $6n_sN_s$ solvent generalized phase space coordinates by $p_v v$ and $p_w w$. For even greater brevity we will collectively denote these generalized coordinates by $S \equiv (p_v v, p_w w)$. The solvent phase space volume element will correspondingly be denoted by $dS = dp_v\, dv\, dp_w\, dw$.

We will subsequently require the Hamiltonian of the solvent conditional that the solute is fixed at configuration point r_0. This Hamiltonian written in generalized coordinates will be denoted by $K[S;r_0]$ where

$$K[S;r_0] = \sum_{\lambda=1}\left\{T_\lambda\left[p_{v_\lambda}v_\lambda, p_{w_\lambda}w_\lambda\right] + K_V[v_\lambda w_\lambda]\right\}$$
$$+ K_{VV}[vw] + K_{VU}[vwr_0] \tag{3.1}$$

with $K_V[v_\lambda w_\lambda]$ = intramolecular potential energy surface of solvent molecule λ, $K_{VV}[vw]$ = intermolecular solvent potential, $K_{VU}[vwr_0]$ = solute–solvent potential, and T_λ = kinetic energy of solvent molecule λ expressed in generalized coordinates.[11]

The solvent canonical ensemble distribution function conditional that the solute is fixed at configuration point r_0 is consequently

$$f_{CA}[r_0] = Z^{-1}[r_0]\exp[-\beta K[S;r_0]], \tag{3.2}$$

where $Z[r_0] = \int \exp[\beta K[S;r_0]]dS$. Finally the corresponding solvent Liouville operator is

$$iL[r_0] = \sum_{\lambda=1}^{N_s}\sum_{i=1}^{r}\left\{\frac{\partial K[S;r_0]}{\partial p_{v_{\lambda i}}}\frac{\partial}{\partial v_{\lambda i}} - \frac{\partial K[S;r_0]}{\partial v_{\lambda i}}\frac{\partial}{\partial p_{v_{\lambda i}}}\right\}$$

$$+ \sum_{\lambda=1}^{N_s}\sum_{i=1}^{r}\left\{\frac{\partial K[S;r_0]}{\partial p_{v_{\lambda i}}}\frac{\partial}{\partial v_{\lambda i}} - \frac{\partial K[S;r_0]}{\partial v_{\lambda i}}\frac{\partial}{\partial p_{v_{\lambda i}}}\right\}. \tag{3.3}$$

Given these preliminaries we now turn to the development of Eq. (3.23). We will use the notation and definitions of Ref. 1 with one modification. The statistics and dynamics of the solvent will be described in generalized, rather than Cartesian, phase space coordinates. Given this modification the notation of Ref. 1 for the temporal development of arbitrary solvent dynamical variables $A[t;r_0]$, for equilibrium averages $\langle A\rangle_{r_0}$, and for time correlation functions $\langle A(t+\tau)A(t)\rangle_{r_0}$ is to be reinterpreted as follows:

$$A[t;r_0]\equiv\exp[iL[r_0]t]A[S;r_0], \tag{3.4a}$$

$$\langle A\rangle_{r_0}\equiv\int f_{CA}[S;r_0]\,A[S;r_0]dS, \tag{3.4b}$$

$$\langle A(t+\tau)B(\tau)\rangle_{r_0}\equiv\int f_{CA}[S;r_0]\,[\exp[iL[r_0]t]$$
$$\times A[S;r_0]]B[S;r_0]\,dS, \tag{3.4c}$$

where $f_{CA}[S;r_0]$ and $iL[R_0]$ are defined in Eqs. (3.2) and (3.3).

C. The gas phase and liquid state forces

Equation (3.23) is constructed from the gas phase and liquid state forces exerted on the solute atoms. These are, respectively, the following $3n$-dimensional column vectors:

$$F_g[r_0] = -\frac{\partial K_{UU}[r_0]}{\partial r_0},$$

$$F_{r_0}[vwr_0] = -\frac{\partial K_{VU}[vwr_0]}{\partial r_0}, \tag{3.5}$$

where $K_{UU}[r_0]$ is the solute gas phase potential energy surface and where $K_{UV}[vwr_0]$ is the solute–solvent potential energy function.

D. A generalized Langevin equation of motion

Our starting point for the development of Eq. (3.23) is a generalized Langevin equation, developed in Ref. 1, which governs the motion of the solute configuration point r_0 in either monatomic or molecular solvents.

This equation of motion written in matrix notation[14] is

$$m^{1/2}\ddot{r}_0(t)m^{1/2} = \langle F \rangle_{r_0} - m^{1/2}[\omega_{e_0}^2[r_0(t)]]m^{1/2}r_0(t)$$
$$+ \int_0^t m^{1/2}[\omega_{c_1}^2[r_0(\tau)]]\theta_1[t-\tau;r_0(\tau)][\omega_{c_1}^2[r_0(\tau)]]^T$$
$$\times m^{1/2}r_0(\tau)d\tau + m^{1/2}\omega_{c_1}^2[r_0(t)]m^{1/2}R_1[t;r_0(t)], \quad (3.6)$$

where the mean force $\langle F \rangle_{r_0}$ is defined by

$$\langle F \rangle_{r_0} = F_g[r_0] + \langle \mathscr{F}_{r_0} \rangle_{r_0}. \quad (3.7)$$

The physical meaning of the forces appearing in Eq. (3.6) have been discussed in detail elsewhere.[1] Briefly stated, the first three terms on the right-hand side of Eq. (3.6) are forces exerted by the average local solvent density. These govern, respectively (see the Introduction): the static solvent effect, the instantaneous dynamic solvent effect, and the delayed dynamic solvent effect. The fourth term is a random force which describes the influence of fluctuations of the local solvent density from its equilibrium value.

The average random solvent forces are interrelated by the following fluctuation–dissipation theorem[1]:

$$\dot{\theta}_1[t;r_0] = [k_B T]^{-1}m^{1/2}\langle \dot{R}_1(t+\tau)\dot{R}_1^T(\tau)\rangle_{r_0}m^{1/2}. \quad (3.8)$$

Equation (3.8) guarantees that solute–solvent energy exchange processes balance so as to maintain or restore thermal equilibrium in the solute system.

E. Molecular formulas

We next present molecular formulas which permit the construction of the solvent forces appearing in Eq. (3.6). The average solvent forces are determined by the following $(3n \times 3n)$-dimensional matrices:

$$\omega_{e_0}^2(r_0) = -m^{1/2}\left\langle \frac{\partial \mathscr{F}_{r_0}^T}{\partial r_0} \right\rangle_{r_0} m^{-1/2}, \quad (3.9a)$$

$$\dot{\theta}_1[t;r_0] = \langle \mathscr{F}_{r_0}\mathscr{F}_{r_0}^T \rangle_{r_0}^{-1/2}\langle \mathscr{F}_{r_0}(t+\tau)$$
$$\times \mathscr{F}_{r_0}^T(\tau)\rangle_{r_0}\langle \mathscr{F}_{r_0}\mathscr{F}_{r_0}^T \rangle_{r_0}^{-1/2}, \quad (3.9b)$$

$$\omega_{c_1}^2(r_0) = [k_B T]^{-1/2}m^{-1/2}\langle \mathscr{F}_{r_0}\mathscr{F}_{r_0}^T \rangle_{r_0}^{1/2}, \quad (3.9c)$$

where the fluctuating solvent force $\mathscr{F}[t;r_0]$ is defined as follows:

$$\mathscr{F}[t;r_0] \equiv \exp[iL[r_0]t]\mathscr{F}_{r_0}[vwr_0] - \langle \mathscr{F}_{r_0}\rangle_{r_0}.$$

The random solvent forces are determined from the $3n$-dimensional column vector $R_1[t;r_0]$ via the relationship

$$R_1[t;r_0] = [k_B T]^{1/2}m^{-1/2}\langle \mathscr{F}_{r_0}\mathscr{F}_{r_0}^T \rangle_{r_0}^{-1/2}\mathscr{F}_{r_0}[t;r_0] \quad (3.10a)$$

or equivalently

$$m^{1/2}\omega_{c_1}^2(r_0)m^{1/2}R_1[t;r_0] = \mathscr{F}[t;r_0]. \quad (3.10b)$$

F. Acoustical and optical contributions to the fluctuating solvent force

We begin the development of Eq. (3.23) from Eq. (3.6) by separating $\mathscr{F}[t;r_0]$ into $r+1$ individual TR and V contribu-

tions. To do this we expand the initial fluctuating force $\mathscr{F}_{r_0}[vwr_0] \equiv \mathscr{F}_{r_0}[vwr_0] - \langle \mathscr{F}_{r_0}\rangle_{r_0}$ to linear order in the mass-weighted displacements from vibrational equilibrium y_{λ_i}. These are defined by

$$y_{\lambda i} = [M_{vv}^{-1/2}]_{ii}[v_{\lambda i} - v_{0\lambda i}], \quad (3.11)$$

where $v_{0\lambda i}$ is the liquid state equilibrium value[11] of the ith normal mode coordinate of solvent molecule λ and where M_{vv} is the vibrational mass matrix defined in Ref. 11. The expansion of $\mathscr{F}_{r_0}[vwr_0]$ is

$$\mathscr{F}_{r_0}[vwr_0] \cong \mathscr{F}_{r_0}[v_0wr_0]$$
$$+ \sum_{\lambda=1}^{N_s}\sum_{i=1}^r \left[\frac{\partial \mathscr{F}_{r_0}}{\partial v_{\lambda i}} \right]_{v=v_0} [M_{vv}^{-1/2}]_{ii}y_{\lambda i}, \quad (3.12)$$

where v_0 denotes the equilibrium values of the V coordinates of the full solvent.

We next define r N_s-dimensional column vectors y_i. These describe the collective vibrational displacements of the solvent associated with the ith normal mode. The y_i are defined by

$$y_i = \begin{bmatrix} y_{1i} \\ y_{2i} \\ \cdot \\ \cdot \\ \cdot \\ y_{N_s i} \end{bmatrix}. \quad (3.13a)$$

We correspondingly define the rN_s-dimensional row vectors $\partial \mathscr{F}_{r_0}/\partial v_i^T$ by

$$\frac{\partial \mathscr{F}_{r_0}}{\partial v_i^T} = \left(\frac{\partial \mathscr{F}_{r_0}}{\partial v_{1i}} \frac{\partial \mathscr{F}_{r_0}}{\partial v_{2i}} \cdots \frac{\partial \mathscr{F}_{r_0}}{\partial v_{N_s i}} \right). \quad (3.13b)$$

Using the vector notation of Eqs. (3.13), Eq. (3.12) may be written in terms of the collective vibrational displacements y_{λ_i} as

$$\mathscr{F}_{r_0}[vwr_0] = \mathscr{F}_{r_0}[v_0wr_0] + \sum_{i=1}^r \left[\frac{\partial \mathscr{F}_{r_0}}{\partial V_i^T} \right]_{v=v_0}$$
$$\times [M_{vv}^{-1/2}]_{ii}y_i. \quad (3.14)$$

Applying $\exp[iL(r_0)t]$ to Eq. (3.13) yields the following expansion of the fluctuating force:

$$\mathscr{F}_{r_0}[t;r_0] = \sum_{s=1}^{r+1} F_s[t;r_0], \quad (3.15)$$

where

$$F_1[t;r_0] = \exp[iL[r_0]t]\,[\mathscr{F}_{r_0}[v_0wr_0]] \quad (3.16a)$$

is the contribution to the fluctuating force arising from *rigid solvent* TR motions and where

$$F_i[t;r_0] = \exp[iL[r_0]t]\,[iL[r_0]T]\left[\left[\frac{\partial \mathscr{F}_{r_0}}{\partial v_i^T} \right]_{v=v_0} \right.$$
$$\left. \times [M_{vv}^{-1/2}]_{ii}y_i \right],$$

$$i = 1, 2, \ldots, r \quad (3.16b)$$

is the contribution arising from collective V motions asso-

ciated with the ith normal mode.

In the remainder of this section, we will utilize the concise supermatrix notation described in Sec. II. In this notation we will collectively represent the fluctuating force components $F_s[t;r_0]$ [Eqs. (3.16) and (3.17)], which are $3n$-dimensional vectors, by the following $(r+1)$-dimensional supervector:

$$\mathbf{F}[t;r_0] = \begin{bmatrix} F_1[t;r_0] \\ F_2[t;r_0] \\ \cdot \\ \cdot \\ \cdot \\ F_{r+1}[t;r_0] \end{bmatrix}. \qquad (3.17)$$

The equivalent chain equations (2.1) may be constructed from the (supermatrix) autocorrelation of the fluctuating solvent force $\langle \mathbf{F}(t+\tau)\mathbf{F}(\tau)\rangle_{r_0}$ by the procedure discussed in the Appendix.

G. The quantities describing partial solvent influence

The next step in the development of Eq. (3.23) is the decomposition of the delayed and random solvent forces into partial contributions associated with the $r+1$ modes of solvent motion.

We will, in particular, decompose the quantities $\omega_{c_i}^2(r_0)$, $\theta_1[t;r_0]$, and $R_1[t;r_0]$ [see Eqs. (3.9) and (3.10)] into partial contributions $[\omega_{c_i}^2(r_0)]_s$, $[\theta_1[t;r_0]]_{st}$ ($3n \times 3n$-dimensional matrices), and $[R_1[t;r_0]]_s$ ($3n$-dimensional vectors).

The mathematical properties of these partial quantities is most evident if we express them in supermatrix notation. Specifically we collect the components $[\omega_{c_i}^2(r_0)]_s$ and $[R_1[t;r_0]]_s$ into the $(r+1)$-dimensional supervectors $\omega_{c_i}^2(r_0)$ and $\mathbf{R}_1[t;r_0]$ defined by

$$\omega_{c_i}^2(r_0) = ([\omega_{c_i}^2(r_0)]_1 [\omega_{c_i}^2(r_0)]_2 \cdots [\omega_{c_i}^2(r_0)]_{r+1}), \qquad (3.18a)$$

$$\mathbf{R}_1[t;r_0] = \begin{bmatrix} [R_1[t;r_0]]_1 \\ [R_1[t;r_0]]_2 \\ \cdot \\ \cdot \\ \cdot \\ [R_1[t;r_0]]_{r+1} \end{bmatrix}. \qquad (3.18b)$$

We will also introduce the $(r+1) \times (r+1)$-dimensional supermatrix $\theta_1[t;r_0]$. The st th element of $\theta_1[t;r_0]$ is the response function $[\theta_1[t;r_0]]_{st}$.

We have not yet given the molecular definitions of the partial quantities. These parallel the definitions of the corresponding full quantities given in Eqs. (3.9) and (3.10). Specifically we define

$$\dot{\theta}_1[t;r_0] = \langle\dot{\mathbf{F}}\dot{\mathbf{F}}^T\rangle_{r_0}^{-1/2}\langle\dot{\mathbf{F}}(t+\tau)\dot{\mathbf{F}}^T(\tau)\rangle_{r_0}\langle\dot{\mathbf{F}}\dot{\mathbf{F}}^T\rangle_{r_0}^{-1/2}, \qquad (3.19a)$$

$$\omega_{c_i}^2(r_0) = [k_B T]^{-1/2}m^{-1/2}\mathbf{1}\langle\dot{\mathbf{F}}\dot{\mathbf{F}}^T\rangle_{r_0}^{1/2}, \qquad (3.19b)$$

and

$$\mathbf{R}_1[t;r_0] = [k_B T]^{1/2}m^{-1/2}\langle\dot{\mathbf{F}}\dot{\mathbf{F}}^T\rangle_{r_0}^{-1/2}\mathbf{F}[t;r_0], \qquad (3.20a)$$

where $\mathbf{1} = (1\ 1\ldots 1)$ in Eq. (3.19b) is the unit row supervector whose elements 1 are the $3n \times 3n$-dimensional unit matrix. The following additional relationships, analogous to Eqs. (3.8) and (3.10b), follow from Eqs. (3.19) and (3.20):

$$m^{1/2}\omega_{c_i}^2(r_0)^{1/2}\mathbf{R}_1[t;r_0]$$
$$= \mathcal{F}_{r_0}[t;r_0] = \sum_{s=1}^{r+1} F_s[t;r_0], \qquad (3.20b)$$

$$\theta_1[t;r_0] = [k_B T]^{-1}m^{1/2}\langle\dot{\mathbf{R}}_1(t+\tau)\dot{\mathbf{R}}_1^T(\tau)\rangle_{r_0}m^{1/2}. \qquad (3.21)$$

From Eqs. (3.8)–(3.10) and (3.19)–(3.21) one may derive the following three identities relating the partial quantities $\omega_{c_i}^2(r_0)$, $\mathbf{R}_1[t;r_0]$, and $\theta_1[t;r_0]$ to the corresponding full quantities $\omega_{c_i}^2(r_0)$, $R_1[t;r_0]$, and $\theta_1[t;r_0]$:

$$m^{1/2}[\omega_{c_i}^2(r_0)]m^{1/2}\mathbf{R}_1[t;r_0]$$
$$= m^{1/2}[\omega_{c_i}^2(r_0)]m^{1/2}R_1[t;r_0], \qquad (3.22a)$$

$$[\omega_{c_i}^2(r_0)]\dot{\theta}_1[t;r_0][\omega_{c_i}^2(r_0)]^T$$
$$= [\omega_{c_i}^2(r_0)]\dot{\theta}_1[t;r_0][\omega_{c_i}^2(r_0)]^T, \qquad (3.22b)$$

$$\omega_{c_i}^4(r_0) \equiv [\omega_{c_i}^2(r_0)][\omega_{c_i}^2(r_0)]^T = \sum_{s=1}^{r+1}[\omega_{c_i}^2(r_0)]_s[\omega_{c_i}^2(r_0)]_s^T$$

$$\equiv \sum_{s=1}^{r+1}[\omega_{c_i}^4(r_0)]_s. \qquad (3.22c)$$

Note that $[\omega_{c_i}^4(r_0)]_s$ may be interpreted as a coupling constant linking the solute motion to the sth mode of solvent motion. Equation (3.22c) thus shows that the full coupling constant $\omega_{c_i}^4(r_0)$ is equal to the sum of the $r+1$ partial coupling constants $[\omega_{c_i}^4(r_0)]_s$.

H. Separation of the effects of acoustical optical fluctuations in the generalized Langevin equation

The generalized Langevin equation of motion [Eq. (3.6)] may be written in the following form using Eqs. (3.22):

$$m^{1/2}\ddot{r}_0(t)m^{1/2} = \langle F\rangle_{r_0(t)} - m^{1/2}\omega_{e_0}^2[r_0(t)]m^{1/2}r_0(t)$$
$$+ \int_0^t m^{1/2}[\omega_{c_i}^2[r_0(t)]]\theta_1[t-\tau;r_0(\tau)][\omega_{c_i}^2[r_0(t)]]^T$$
$$\times m^{1/2}r_0(\tau)d\tau + m^{1/2}\omega_{c_i}^2[r_0(t)]m^{1/2}\mathbf{R}_1[t;r_0(t)]. \qquad (3.23)$$

Equation (3.23) provides the required separation of temporal solvent density fluctuations on solute motion into TR and V contributions. The equivalent chain equations (2.1) are derived from Eq. (3.23) in the Appendix.

IV. SUMMARY AND DISCUSSION

In this paper we have developed a generalized Langevin equation framework which permits one to realistically simulate chemical reaction dynamics in molecular solvents.

The main result of this paper is the infinite set of equivalent chain equations, Eq. (2.1), which govern the dynamics of the solute configuration point r_0. These contain a low frequency acoustical branch which simulates the influence of the solvent translational–rotational (TR) density fluctuations and r high frequency optical branches which simulate the influence of the solvent normal mode vibrational (V) density fluctuations. The $r+1$ branches are crosslinked [Fig. 1(b)]. These crosslinks are the chain formalism equivalent of

the physical coupling of all $r + 1$ modes of solvent motion by liquid state effects.

The equivalent chain equations may be systematically approximated to yield a rapidly convergent sequence of effective few-body model equations of motion, Eq. (2.2). These may be conveniently solved by classical trajectory methods.[2(a)] Even the simplest model [$p = 1$ in Eq. (2.2a)] provides a qualitatively realistic description of both the acoustical and optical branches of the solvent frequency spectrum $\sigma_1[\omega;r_0]$. Thus even the simplest model describes solute energy exchange with all $r + 1$ modes of solvent motion in a qualitatively realistic manner.

The developments in this paper, while based on the formally exact theory of the equivalent chain,[1] additionally involve three physically motivated approximations. These are:

(i) Our starting point [Eq. (3.6)] is based on the approximation of full clamping of the solute configuration point r_0. The justifications for this approximation have been discussed in detail elsewhere.[1,2,13]

(ii) The decomposition of the dynamic solvent response into $r + 1$ contributions [Eq. (3.15)] is based on the implicit assumption that the solvent vibrational motions are harmonic. The harmonic approximation suppresses overtone and combination band contributions to the solvent frequency spectrum. Thus processes[15] whose rates are significantly influenced by these anharmonic bands are beyond the scope of the present treatment.

(iii) The development of the equivalent chain equations from Eq. (3.23) involves the physical assumption that the local equilibrium solvent density does not change appreciably during trajectory segments of subpicosecond time scale duration. As discussed elsewhere,[1,2] this assumption usually realistic at liquid state densities except for extremely rapid processes (e.g., the initial states of photolytic cage escape).

To practically implement the present theory one requires the autocorrelation matrix of the fluctuating solvent force $\langle \mathbf{F}(t + \tau)\mathbf{F}^T(\tau)\rangle_{r_0}$ [see Eq. (3.17)]. We are currently developing approximation methods which permit one to inexpensively construct this quantity from *rigid solvent* pair correlation functions which may be obtained as solutions to integral equations for molecular liquids.

Given this practical method of implementation the present theory will be of value in at least three ways:

(a) The theory provides a new set of theoretical concepts for interpreting solvent effects on chemical processes occurring in molecular liquids. The concepts permit one to obtain considerable insight into the microscopic details of local energy transfer processes which underlie the solvent effects. These insights can be obtained from simple calculations which bypass detailed simulations.

The parameter $[\omega_{c_i}^2(r_0)]_s$, for example, provides a direct measure of the strength of coupling between the solute atoms and the sth [$s = 1,2,...,r + 1$] mode of solvent motion. Moreover, the magnitude of the diagonal spectral density element $[\sigma_1[\omega;r_0]]_{ss}$, evaluated in the chemically relevant range ω_0, provides a measure of the efficiency of the sth mode of solvent motion as a sink for dissipation of solute energy. Therefore the branching ratios

$$R_s = \frac{[\omega_{c_i}^4(r_0)]_s [\sigma_1[\omega_0;r_0]]_{ss}}{\Sigma_{s'}[\omega_{c_i}^4(r_0)]_{s'}[\sigma_1[\omega_0;r_0]]_{s's'}} \qquad (4.1)$$

provide quantitative information about the nature of the local energy disposal. They tell, for example, what fraction of the solute energy is dissipated by the solvent TR degrees of freedom, what fraction by the ith normal mode solvent vibrational degrees of freedom, etc.

As a second example, a determination of the off-diagonal spectral density elements $[\sigma_1[\omega_0;r_0]]_{st}$ provides an immediate insight into the importance of energy redistribution in the solvent cage (in this case energy transfer between the sth and tth modes of solvent motion) in influencing solute dynamics.

(b) The theory in its present form provides the basis for practical methods of simulating the reaction dynamics of small, e.g., diatomic, solutes in molecular solvents. Truncation of the stochastic equations of motion at the p molecule level for an n-atom solute amounts to replacing the physical solvent by an equivalent system composed of $3np(r + 1)$ degrees of freedom. If we assume in a full molecular dynamics calculation ~ 100 solvent molecules are required per solute atom to obtain a realistic representation of the system then a molecular dynamics simulation will require $100n(r + 6)$ solvent degrees of freedom.

As an example, an equivalent chain simulation of iodine photolysis in carbon tetrachloride with the equivalent chain equations truncated at the $p = 2$ level requires the solution of 126 simultaneous equations of motion. A corresponding molecular dynamics simulation requires the solution of 3006 coupled equations of motion.

(c) The theory developed in this paper will become a much more powerful tool both conceptually and calculationally when combined with the method of partial clamping developed elsewhere for solute motion in monatomic solvents.[13] The partial clamping method is based on the following idea:

In order to understand the main features of many liquid state chemical processes, it is only necesssary to follow the dynamics of a small number q of *explicit* solute generalized coordinates. The explicit coordinates, e.g., a normal mode coordination or a reaction coordinate, are ones whose dynamics is of direct chemical interest. The partial clamping method leads to a generalized Langevin equation for the dynamics of the explicit solute coordinates. This equation includes the influence of the remaining $3n$-q implicit solute coordinates as well as the influence of the solvent in a physically realistic manner.

We are currently combining the partial clamping concept with the methods of this paper to provide a generalized Langevin equation framework for dealing with explicit coordinate dynamics in molecular solvents. This framework has the following advantages:

(i) The methods presented in this paper became impractical for polyatomic solutes unless they are combined with the partial clamping concept. This is because the sampling of the $3n$-dimension solute configuration space becomes prohibitively expensive for large n and because the supermatrix chain parameters became of inconveniently large dimension

$3n(r + 1) \times 3n(r + 1)$. If one instead constructs equivalent chain equations for a small number $q = 1$ or 2 of explicit coordinates only a q-dimensional solute configuration space sampling is required. Moreover, the equivalent chain parameters become matrices of small dimension, namely $q(r + 1) \times q(r + 1)$.

Thus the partial clamping method should make the treatment of reaction dynamics of polyatomic solutes in molecular solvents feasible. If, for example, we consider the simple SN_2 reaction $Br^- + CH_3Cl \rightarrow BrCH_3 + Cl^-$ in aqueous solution and take as the single explicit coordinate the reaction coordinate, only a one-dimensional configuration space sampling is required and the equivalent chain parameters are matrices of relatively small dimension, namely 4×4.

Moreover, if one constructs a p-molecule stochastic model for the solute reaction coordinate analogous to Eq. (2.2) for the configuration point, the problem of reaction coordinate dynamics for the aqueous SN_2 reaction requires (for $p = 2$) the solution of *nine* simultaneous equations of motion. Using our previous prescription of 100 solvent molecules/per solute atom (and taking CH_3 as an atom), the corresponding molecular dynamics simulation of the aqueous $Br^- + CH_3Cl$ SN_2 reaction would require the solution of 2709 simultaneous equations of motion.

ACKNOWLEDGMENTS

APPENDIX: DERIVATION OF THE EQUIVALENT CHAIN EQUATIONS FOR MOLECULAR SOLVENTS

We next briefly describe how the equivalent chain equations for molecular solvents, Eq. (2.1), may be developed from the generalized Langevin equation, Eq. (3.23). The development parallels our earlier work restricted to monatomic solvents presented in Chap. 6 of Ref. 1. The present description will, therefore, consist of a brief outline with details of the proofs omitted.

The development is based on the stationarity and time reversal symmetry properties of the fluctuating force autocorrelation matrix $\langle \mathbf{F}(t + \tau)\mathbf{F}^T(\tau)\rangle_{r_0}$. From these properties a hierachy structure may be developed. We now summarize the main results of this structure.

(i) An infinite sequence of $(r + 1) \times (r + 1)$-dimensional supermatrix response functions $\boldsymbol{\theta}_p [t;r_0]$, $p = 2, 3, \ldots$, may be recursively constructed [Eq. (A9)] from the response function $\boldsymbol{\theta}_1[t;r_0]$ defined in Eq. (3.19a). The response functions have the following basic mathematical properties:

$$\dot{\boldsymbol{\theta}}_p [- t;r_0] = \dot{\boldsymbol{\theta}}_p [t;r_0] = \dot{\boldsymbol{\theta}}_p^T[t;r_0],$$
$$\dot{\boldsymbol{\theta}}_p [0;r_0] = 1 \text{ and } \boldsymbol{\theta}_p [0;r_0] = 0, \quad p = 1,2,\ldots, \quad (A1)$$

where 1 and 0 are, respectively, the unit and null supermatrices.

(ii) A corresponding infinite sequence of $(r + 1)$-dimensional supervector coordinate variables $\mathbf{R}_p [t;r_0]$ may be recursively constructed [Eq. (A10)] from the basic variable $\mathbf{R}_1[t;r_0]$ defined in Eq. (3.20a).

(iii) The response functions and coordinate variables are related by fluctuation–dissipation theorems analogous to Eq. (3.21). Explicitly in the notation of Ref. 1,

$$\dot{\boldsymbol{\theta}}_p [t;r_0] = [k_B T]^{-1} m^{1/2} \langle \dot{\mathbf{R}}_p(t + \tau)\dot{\mathbf{R}}_p^T(\tau)\rangle_{r_0,r_1,\ldots,r_{p-1}} m^{1/2}. \quad (A2)$$

(iv) The supermatrix spectral densities $\sigma_p [\omega;r_0]$ of the response functions $\boldsymbol{\theta}_p [t;r_0]$ are defined by the cosine transform relationships

$$\sigma_p [\omega;r_0] = \frac{2}{\pi} \int_0^\infty \cos \omega t \dot{\boldsymbol{\theta}}_p [t;r_0]dt,$$
$$\dot{\boldsymbol{\theta}}_p [t;r_0] = \int_0^\infty \cos \omega t \sigma_p [\omega;r_0]d\omega. \quad (A3)$$

These spectral densities have the following basic mathematical properties:

$$\sigma_p [- \omega;r_0] = \sigma_p [\omega;r_0] = \sigma_p^T[\omega;r_0],$$
$$\sigma_p [\omega;r_0] > 0 \text{ and } \int_0^\infty \sigma_p [\omega;r_0]d\omega = 1, \quad p = 1, 2, \ldots, \quad (A4)$$

where the symbol $>$ denotes positive definiteness. {The positivity of $\sigma_p [\omega;r_0]$ may be proven from Eqs. (A2) and (A3).}

(v) The supermatrix equivalent chain parameters $\{\omega_{e_p}^2(r_0), \omega_{c_{p+1}}^2(r_0)\}$ are defined in terms of the second and fourth moments of $\sigma_p [\omega;r_0]$ via the following relationships:

$$\omega_{e_p}^2(r_0) = \int_0^\infty \omega^2 \sigma_p [\omega;r_0]d\omega,$$
$$\omega_{c_{p+1}}^4(r_0) = \int_0^\infty [\omega^2 1 - \omega_{e_p}^2(r_0)]$$
$$\times \sigma_p [\omega;r_0] [\omega^2 1 - \omega_{e_p}^2(r_0)]^T d\omega, \quad (A5a)$$

and

$$[\omega_{c_{p+1}}^2(r_0)] [\omega_{c_{p+1}}^2(r_0)]^T = \omega_{c_{p+1}}^4(r_0). \quad (A5b)$$

From Eqs. (A4) and (A5) it follows that $\omega_{e_p}^2(r_0)$ and $\omega_{c_{p+1}}^4(r_0)$ have the following symmetry and positivity properties:

$$\omega_{e_p}^2(r_0) = [\omega_{e_p}^2(r_0)]^T > 0,$$
$$\omega_{c_{p+1}}^4(r_0) = [\omega_{c_{p+1}}^4(r_0)]^T > 0. \quad (A6)$$

[From Eq. (A6) it may be proven that the normal mode frequencies of the equivalent chain for molecular solvents are real and that, consequently the equivalent chain equations are mechanically stable.]

(vi) The supermatrix truncation parameters $\boldsymbol{\beta}_{p+1} [r_0]$ and $\boldsymbol{\Omega}_p(r_0)$ are defined in terms of $\boldsymbol{\theta}_p [t;r_0]$ via the relationships

$$\boldsymbol{\beta}_{p+1}(r_0) = \int_0^\infty \boldsymbol{\beta}_{p+1} [t;r_0]dt, \quad (A7a)$$

where

$$\beta_{p+1}[t;r_0] = -\int_0^\infty \left[\omega^2_{c_{p+1}}(r_0)\right]\theta_{p+1}$$
$$\times [\tau;r_0]\left[\omega^2_{c_{p+1}}(r_0)\right]^T d\tau$$

(A7b)

and

$$\Omega_p^{-2}(r_0) = \int_0^\infty \theta_p[t;r_0]dt. \qquad \text{(A8)}$$

(vii) The recursive definition of the infinite sequence of response functions $\theta_p[t;r_0]$ from $\theta_1[t;r_0]$ is

$$\ddot{\theta}_1[t;r_0] = -\omega^2_{e_1}(r_0)\theta_1[t;r_0] + \int_0^t \left[\omega^2_{c_2}(r_0)\right]\theta_2[t-\tau;r_0]$$
$$\times \left[\omega^2_{c_2}(r_0)\right]^T \theta_1[\tau;r_0]d\tau,$$

$$\ddot{\theta}_2[t;r_0] = -\omega^2_{e_2}(r_0)\theta_2[t;r_0] + \int_0^t \left[\omega^2_{c_3}(r_0)\right]\theta_3[t-\tau;r_0]$$
$$\times \left[\omega^2_{c_3}(r_0)\right]^T \theta[\tau;r_0]dt,$$

$\cdot$
$\cdot$
$\cdot$

(A9)

The first member of Eq. (A5) defines $\theta_2[t;r_0]$ in terms of $\theta_1[t;r_0]$, the second member defines $\theta_3[t;r_0]$ in terms of $\theta_2[t;r_0]$, etc.

The corresponding recursive definition of the infinite sequence of coordinate variables $R_p[t;r_0]$ from $R_1[t;r_0]$ is

$$m^{1/2}\ddot{R}_1[t;r_0]m^{1/2} = -m^{1/2}\left[\omega^2_{e_1}(r_0)\right]m^{1/2}R_1[t;r_0]$$
$$+ \int_0^t m^{1/2}\left[\omega^2_{c_2}(r_0)\right]\theta_2[t-\tau;r_0]\left[\omega^2_{c_2}(r_0)\right]^T$$
$$\times m^{1/2}R_1[\tau;r_0]d\tau + m^{1/2}\omega^2_{c_2}(r_0)m^{1/2}[t;r_0],$$

$$m^{1/2}\ddot{R}_2[t;r_0]m^{1/2} = -m^{1/2}\left[\omega^2_{e_2}(r_0)\right]m^{1/2}R_2[t;r_0]$$
$$+ \int_0^t m^{1/2}\left[\omega^2_{c_3}(r_0)\right]\theta_3[t-\tau;r_0]\left[\omega^2_{c_3}(r_0)\right]^T$$
$$\times m^{1/2}R_2[\tau;r_0]dt + m^{1/2}\omega^2_{c_3}(r_0)m^{1/2}R_3[t;r_0],$$

$\cdot$
$\cdot$
$\cdot$

(A10)

(viii) The supervector equivalent chain coordinates [Eq. (2.1)] $r_1(t)$, $r_2(t)$, ... are recursively defined in terms of the solute configuration point $r_0(t)$[14] by the relationships

$$r_1(t) = R_1[t;r_0(t)] + \int_0^t m^{-1/2}\theta_1[t-\tau;r_0(\tau)]$$
$$\times \left[\omega^2_{c_1}[r_0(\tau)]\right]^T m^{1/2}r_0(\tau)d\tau,$$

$$r_2(t) = R_2[t;r_0(t)] + \int_0^t m^{-1/2}\theta_2[t-\tau;r_0(\tau)]$$
$$\times \left[\omega^2_{c_2}[r_0(\tau)]\right]^T m^{1/2}r_1(\tau)d\tau,$$

$\cdot$
$\cdot$
$\cdot$

$$r_p(t) = R_p[t;r_0(t)] + \int_0^t m^{-1/2}\theta_p[t-\tau;r_0(\tau)]$$

$$\times \left[\omega^2_{c_p}[r_0(\tau)]\right]^T m^{1/2}r_{p-1}(\tau)d\tau,$$

$\cdot$
$\cdot$
$\cdot$

(A11)

Given the above results, the derivation of Eq. (2.1) from Eq. (3.23) may be readily carried out via a construction analogous to that presented in Ref. 1. As mentioned in Sec. IV the derivation involves one physical approximation.

Finally to numerically construct the effective few-body models, Eqs. (2.2), for specific solute–solvent systems one requires a practical algorithm which permits one to conveniently compute the supermatrix chain parameters $\{\omega^2_{e_p}(r_0),$ $\omega^2_{c_{p+1}}(r_0)\}$ and the truncation parameters $\{\Omega_p^2(r_0),\beta_{p+1}(r_0)\}$ from the fluctuating force autocorrelation matrix $\langle F(t+\tau) F^T(\tau)\rangle_{r_0}$. Such an algorithm may be readily developed from the results presented in this Appendix. The development parallels the argument presented in Appendix B of Ref. 1 and will, therefore, be omitted here.

[1]MTGLE is an acronym for molecular time scale generalized Langevin equation. For a complete review of the MTGLE theory see S. A. Adelman, Adv. Chem. Phys. **53**, 61 (1983). For a brief review see S. A. Adelman, J. Phys. Chem. **89**, 2213 (1985).

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[6]Static solvent effects arise from the forces exerted by the *equilibrium* local solvent density on *stationary* solute atoms. The net effect of these forces is to modify the gas phase potential energy surface to a liquid state potential of mean force surface. Dynamic solvent effects are corrections to the static effects experienced by moving solute atoms. These arise from the fact that the local solvent density cannot remain in equilibrium with solute atoms moving at a finite rate.

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[13]S. A. Adelman, J. Chem. Phys. **81**, 2776 (1984). The equivalent chain equations for the motion of the explicit solute generalized coordinates are not actually written down in this paper. It is straightforward, however, to derive them from its main results.

derive them from its main results.

[14]If r_{0i} and m_i are, respectively, the Cartesian coordinates and mass of solute atom i then the solute configuration point r_0 and the solute mass matrix m are defined by

$$r_0 = \begin{bmatrix} r_{01} \\ r_{02} \\ \cdot \\ \cdot \\ \cdot \\ r_{0n} \end{bmatrix}$$

and

$$m = \begin{bmatrix} m_1 & & & & & & \\ & m_1 & & & & \bigcirc & \\ & & m_1 & & & & \\ & & & m_{n-1} & & & \\ & \bigcirc & & & m_n & & \\ & & & & & m_n & \\ & & & & & & m_n \end{bmatrix}.$$

[15]An example is the liquid state quenching of the $^1\Delta$ state of molecular oxygen as described in P. B. Merkel and D. R. Kearns, J. Am. Chem. Soc. **94**, 7244 (1972).

[16]This idea was suggested to us by the gas phase work of Marcus and Miller. See for example, R. A. Marcus, J.Chem. Phys. **49**, 2617 (1968); W. H. Miller, *ibid*. **72**, 99 (1980).