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Generalized Langevin theory for many-body problems in chemical dynamics: The method of partial clamping and formulation of the solute equations of motion in generalized coordinates

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A formulation of the analytical dynamics of an n -atom solute system present at infinite dilution in a monatomic solvent is presented. This treatment, which will aid in the understanding of liquid state spectroscopic, energy-transfer, and chemical reaction processes, is made by combining the methods of classical dynamics with recently developed generalized Langevin equation techniques [S. A. Adelman, *Adv. Chem. Phys.* **53**, 611 (1983)]. The Hamiltonian of the solute system is formulated in generalized coordinates which are related to the underlying Cartesian coordinates by a point canonical transformation. The $3n$ generalized coordinates are partitioned into a set of p explicit coordinates whose dynamics are of direct interest and a set of $q = 3n - p$ implicit coordinates whose motion is of lesser interest. A generalized Langevin equation of motion for the explicit coordinates is formulated by computing the reaction force exerted by the solvent on the explicit coordinates in response to small displacements of these coordinates. This generalized Langevin equation will provide a realistic description of explicit coordinate dynamics if the liquid state motion of these coordinates is oscillatory on subpicosecond time scales. Solvent effects appearing in the generalized Langevin equation may be discussed in terms of the fluctuation spectrum which describes atomic motion in the solvation shells. A rigorous statistical mechanical method for assessing the influence of the implicit coordinate motion on this fluctuation spectrum is presented. The formulas for the liquid state quantities appearing in the generalized Langevin equation may be exactly evaluated for particular solute-solvent systems via molecular dynamics (MD) simulation of the motion of the implicit and solvent coordinates given that the solute is partially clamped, i.e., given that the explicit coordinates are fixed. The method of partial clamping provides an improvement of the method of full solute clamping developed earlier. This improvement should permit one to realistically treat many liquid state processes via generalized Langevin equation techniques for which the solute/solvent mass ratio is less than unity.

I. INTRODUCTION

Recently we have presented¹ a quite general conceptual and calculational framework for simplifying the many-body problems which complicate the theoretical treatment of spectroscopic,² energy transfer,³ and chemical reaction⁴ processes in condensed phases. This framework which we call the MTGLE theory is based on the modern statistical mechanical theory of irreversible processes.⁵⁻⁷

The MTGLE theory has been developed in considerable detail¹ for the case of liquid state chemical reactions. For that case the theory provides a rigorous framework which permits one to conveniently and quantitatively implement the following qualitative strategy for simplifying problems in liquid state chemical kinetics: Treat the influence of the first one or two solvation shells on the solute in detail; model the influence of the solvent external to these shells by that of a macroscopic energy reservoir.

This theory of liquid solution reactions¹ has recently been applied to study, via the method of stochastic classical trajectories,⁸ a prototype liquid state photochemical reaction; namely the photodissociation and subsequent geminate recombination of molecular iodine in simple solvents.⁹ Application of the theory to other basic problems in condensed phase chemical kinetics is underway.¹⁰

These first applications and related work¹¹ have

brought out a number of important aspects of condensed phase chemical reaction dynamics. The most important point brought out by the simulations, from the viewpoint of the present work, concerns the basic role played by temporal density fluctuations in the solvation shells in influencing solute dynamics. The nature of the frequency spectrum¹² which describes these fluctuations, in particular, importantly influences the rate of local solute energy dissipation and hence the course of liquid solutions processes. (Qualitatively speaking, local energy dissipation is efficient if solvation shell and relevant solute frequencies are in near resonance.)

These first applications, moreover, while making apparent the value of the MTGLE theory as an interpretive and calculational tool for condensed phase chemical kinetics also made clear the need for further development and refinement. The developments and refinements dealt with in this paper concern the following points:

(i) In the theory of liquid solution reactions developed in Ref. 1, the frequency spectrum describing solvation shell density fluctuations is determined within a model which we call the *clamping approximation*. This model, which is exact for a number of limiting cases,¹³ is formally analogous to the gas-phase Born-Oppenheimer approximation. Moreover, it has a deep justification in the mathematical structure of the MTGLE theory.¹⁴

Within this model one assumes that the *random* solvent

forces exerted on the solute atoms when they are located at configuration point r_0 may be approximated by the solvent forces exerted on these atoms given that they are *fixed* at point r_0 . Thus within the clamping approximation one ignores the effects of solute reaction to solvent motion when constructing the random forces. The effects of this reaction are, however, included in the systematic solvent forces exerted on the solute.

The clamping approximation is expected to be a good one if the solute atoms make only small excursions from configuration point r_0 on a time scale comparable to a solvent atom velocity relaxation time. This often occurs at liquid state densities, since solute motion can be highly hindered at these densities, if the solute atom/solvent molecular mass ratio is greater than unity. The clamping approximation, however, may break down for solute/solvent mass ratios which are less than unity even at liquid state densities.¹⁵

While the assumption that the full solute configuration makes only small excursions on a subpicosecond time scale may frequently break down,¹⁶ the more restricted assumption that certain solute degrees of freedom make such small excursions may be much more realistic. For example, consider the dynamics of a low mass and high vibrational frequency diatomic molecule dissolved in a massive monatomic solvent (e.g., molecular nitrogen dissolved in liquid xenon). The assumption that the vibrational coordinate of the molecule executes small amplitude motions may be far more realistic than the assumption that the full configuration point executes such motions.

One of the refinements dealt with in this paper is the lifting of the assumption of full solute clamping when calculating the solvation shell fluctuation spectrum. Instead we introduce the more refined approximation of *partial solute clamping* in which only those solute degrees of freedom which make small excursions are fixed while the remaining degrees of freedom are allowed to move freely in the liquid. Thus for our earlier example of molecular nitrogen in liquid xenon, one might wish to fix the solute vibrational coordinate at its gas-phase equilibrium value while allowing the center of mass and rotational coordinates to move without constraint in the liquid.

We expect that this method of partial clamping will permit one to treat at a reasonable level of realism many liquid state chemical processes for which the solute/solvent mass ratio is less than unity.

(ii) To utilize the methods of Ref. 1, one must construct solvent response function surfaces somewhat analogous to gas-phase Born–Oppenheimer potential energy surfaces. These response function surfaces are, in essence, time-domain transforms of the solvation shell fluctuation spectrum.

For an n -atom solute, these surfaces are, in general, matrices of dimension $9n^2$ and are functions of the solute configuration point, a vector of dimension $3n$. (Symmetry considerations, however, often lead to great simplification.¹⁷) For small, say diatomic, solutes both the construction of these surfaces and their physical interpretation is straightforward.^{1,11} For polyatomic solutes, however, the construction becomes more laborious and the physical interpretation less transparent.

Moreover, there are many experiments which *directly* probe the dynamics of only one or a few solute degrees of freedom. We will refer to these as the *explicit* solute degrees of freedom. The remaining solute coordinates will be referred to as the *implicit* solute degrees of freedom. For example, a measurement of the energy relaxation time of a particular normal mode in a polyatomic solute molecule probes the dynamics of that mode which, for this case, is the explicit coordinate.¹⁸ The remaining implicit coordinates are the other normal modes and the center of mass and rotational coordinates. As a second example, measurement of a chemical rate constant of a molecule directly probes the motion of its reaction coordinate¹⁹ which is the explicit coordinate. The orthogonal modes¹⁹ and the molecular framework translational-rotational coordinates are, for this case, the implicit degrees of freedom.

Given this discussion, it is clear that it would be desirable to develop a reduced equation of motion describing the dynamics of the explicit coordinates. The advantages of such a reduced description include:

(a) For the case of a single explicit coordinate, the response function surface which describes the influence of solvation shell fluctuations on that coordinate is of easily interpretable one-dimensional form.

(b) The equation of motion for a single explicit coordinate can often be solved analytically²⁰ to yield simple results for, say, the rate of vibrational energy relaxation³ of a particular normal mode or the rate of barrier crossing of a reaction coordinate.²¹ Such analytic results should be useful in correlating experimental data.

We wish to stress that any realistic reduced description of explicit coordinate dynamics must account for modification of the relevant solvent fluctuation spectrum due to implicit coordinate motion. For example, if the explicit degree of freedom is the vibrational mode of a diatomic molecule and the implicit degrees of freedom are its translation-rotational coordinates then the *solvent* fluctuation spectrum for the vibrational mode has spectral weight near the frequencies of the hindered translational-rotational motion of the molecule. This modification of the solvent spectrum must be included in order to account for the competition between processes which are, in part, intramolecular and processes which are direct. For example, vibrational energy relaxation of a particular normal mode may proceed via an intramolecular mechanism (explicit mode \rightarrow implicit modes \rightarrow solvent) or via a direct mechanism (explicit mode \rightarrow solvent).

This paper is concerned with the development of a sophisticated reduced description for the explicit coordinate dynamics and with the associated concept of partial clamping.

We consider a solute system composed of n atoms immersed, for simplicity, in a monatomic solvent. This solute system may consist of just the reagent atoms or it may include the reagent atoms and a surrounding sheath of solvent molecules.²² The instantaneous configuration point of the solute system may be described by its $3n$ Cartesian coordinates $r_0 = (r_{01}, \dots, r_{0n})$. Alternatively the configuration point may be described by a set of $3n$ generalized coordinates $x_0 = (x_{01}, \dots, x_{03n})$. We will assume in this paper that the Car-

tesian and generalized coordinates are related by a point canonical transformation.²³ Thus $x_0 = x_0[r_0]$. The solute generalized coordinates $x_0[r_0]$ may be further partitioned into a set of q explicit coordinates $y_0[r_0]$, whose dynamics is of direct interest, and a set of $p = 3n - q$ implicit coordinates $z_0[r_0]$ whose dynamics is of less interest.

In Sec. II we formulate the Hamiltonian of the liquid solution in terms of the generalized coordinates $y_0[r_0]$ and $z_0[r_0]$. A reduced equation of motion of generalized Langevin form for the explicit coordinates $y_0[r_0]$ is formulated in Appendix A and presented and discussed in Sec. III.

Derivation of the molecular formulas for the liquid state quantities appearing in the generalized Langevin equation of motion is given in Sec. V. This derivation, which is based on linear response theory,^{5(a)} uses results developed in Appendix B. The derivation is based on the assumption that the coordinates y_0 are executing small forced displacements and thus requires one to consider the problem of classical dynamics in the presence of constraints. This problem is discussed in Sec. IV.

In Sec. VI and Appendix C, a rigorous statistical mechanical method is presented for assessing the influence of the implicit coordinate motion on the solvent fluctuation spectrum for the explicit coordinates. This method, as we expect to show in subsequent papers, should permit one to estimate the relative rates of intramolecular and direct processes by analytic methods, i.e., without detailed simulation. A brief summary is given in Sec. VII.

The formulas for the liquid state quantities presented in Sec. V may be evaluated for particular solute-solvent systems via molecular dynamics (MD) simulation of the motion of the implicit and solvent coordinates given that the solute is *partially clamped*, i.e., given that the explicit coordinates are fixed. Approximate formulas²⁴ which permit one to evaluate these quantities from equilibrium pair correlation functions may be developed using the Kirkwood superposition approximation. The development parallels one presented elsewhere¹ and thus will be omitted here.

We plan to soon present applications of the general theory developed in this paper to the calculation of molecular spectra, vibrational energy relaxation rates, and barrier crossing rates for specific solute-solvent systems.

II. CANONICAL EQUATIONS OF MOTION

A. Specification of the liquid solution

We begin with a specification of the liquid solution. We assume an s -component monatomic solvent. Present in this solvent at infinite dilution is an n -atom solute system. If one is interested in the molecular spectroscopy, vibrational energy relaxation, or unimolecular kinetics of a particular molecule, the solute system will normally consist of that molecule. If one is interested in the bimolecular kinetics of a pair of molecules, the solute system will usually consist of that pair. The solute system, however, may in principle include, in addition to the molecules of direct chemical interest, a cluster of neighboring solvent molecules.²²

We will denote the mass, Cartesian coordinate, and Cartesian momentum of solute molecule i by, respectively, m_i , r_{0i} , and $p_{0i} = m_i \dot{r}_{0i}$. We will correspondingly denote the

mass, coordinate, and momentum of the λ th solvent atom of species α by M_α , $q_{\lambda\alpha}$, and $p_{\lambda\alpha}$.

We assume that solvent species α consists of N_α atoms. The number concentration of species α will be denoted by $\rho_\alpha = V^{-1}N_\alpha$, where V is the volume of the solution. The Kelvin temperature of the solution will be denoted by T . Thus the thermodynamic state of the solution is characterized by the set of number concentrations ρ_α , $\alpha = 1, 2, \dots, s$, and the Kelvin temperature T .

For brevity, we will often collectively denote the solute and solvent phase space coordinates by the column vectors $r_0 p_0$ and $q p_q$.²⁵ The solute atom masses will, correspondingly, be denoted by the diagonal matrix m .²⁵

The classical Hamiltonian of the solution may be written using this concise notation as

$$H[p_0 r_0, p_q q] = H_{UU}[p_0 r_0] + H_{VV}[p_q q] + U_{VU}[q r_0]. \quad (2.1)$$

Note that $H_{UU}[p_0 r_0]$ is the gas-phase Hamiltonian of the solute system, $H_{VV}[p_q q]$ is the Hamiltonian of the pure solvent, and $U_{VU}[q r_0]$ is the solute-solvent potential energy function.

The gas-phase solute Hamiltonian is

$$H_{UU}[p_0 r_0] = \sum_{i=1}^n \frac{p_{0i} \cdot p_{0i}}{2m_i} + U_{UU}[r_0], \quad (2.2)$$

where $U_{UU}[r_0]$ is the gas-phase potential energy surface of the solute system.

The pure solvent Hamiltonian is, correspondingly,

$$H_{VV}[p_q q] = \sum_{\alpha=1}^s \sum_{\lambda=1}^{N_\alpha} \frac{p_{\lambda\alpha} \cdot p_{\lambda\alpha}}{2M_\alpha} + U_{VV}[q], \quad (2.3)$$

where $U_{VV}[q]$ is the pure solvent potential energy function.

B. Solute Hamiltonian in generalized coordinates

We have indicated that it is often advantageous to analyze the solute motion in generalized coordinates. Thus we next transform from the $6n$ Cartesian phase space coordinates to a new set of $6n$ canonical²³ phase space coordinates. In shorthand vector notation,²⁵ these generalized coordinates will be denoted by $x_0 p_{x_0}$.

We assume the new canonical coordinates are linked to the Cartesian coordinates by a time-independent point transformation. For this case, the new coordinates x_0 are functions of only the old coordinates r_0 , i.e.,

$$x_0 = x_0[r_0] \quad \text{or} \quad r_0 = r_0[x_0]. \quad (2.4)$$

The special case of point transformations includes many of the generalized coordinate systems important in chemical kinetics and molecular spectroscopy. Examples include familiar systems like center of mass, rotational, and internal coordinates,¹⁸ bond angle and bond displacement coordinates,¹⁸ and natural collision coordinates.¹⁹

However other systems important in chemistry, e.g., action-angle variable systems,²³ are related to the Cartesian coordinates by more general canonical transformations. Such coordinate systems are outside the scope of this article.

Given the transformation relations of Eq. (2.5), it is straightforward to develop an expression for the Hamiltonian

ian of the liquid expressed in terms of generalized coordinates. We will denote this Hamiltonian by $K[p_{x_0}, x_0, p_q, q] \equiv H[p_{x_0}, p_q, q]$. This expression is based on the following result²⁶ for the kinetic energy of the solute T_{UU} expressed in terms of the generalized coordinates and velocities

$$T_{UU} = \sum_{i=1}^n \frac{\mathbf{p}_{0i} \cdot \mathbf{p}_{0i}}{2m_i} = \frac{1}{2} \dot{x}_0^T m[x_0] \dot{x}_0. \quad (2.5)$$

(Note here and below the symbol T denotes a vector or matrix transpose.)

The solute mass matrix $m[x_0]$ appearing in Eq. (2.5) is a $3n \times 3n$ symmetric matrix whose elements are defined by

$$m_{ij}[x_0] = m_{ji}[x_0] = \sum_{k=1}^n m_k \frac{\partial \mathbf{r}_{0k}[x_0]}{\partial x_{0i}} \cdot \frac{\partial \mathbf{r}_{0k}[x_0]}{\partial x_{0j}}. \quad (2.6)$$

The x_0 dependence of the mass matrix $m[x_0]$ arises because the coordinate transformation $\mathbf{r}_0 \rightarrow x_0$ is, in general, nonlinear. The x_0 coordinates thus form a curvilinear system. A physical consequence is that centripetal-like forces act on the degrees of freedom x_0 .

The conjugate generalized momenta p_{x_0} may be constructed from Eq. (2.5) using the relationship $p_{x_0} = (\partial T_{UU} / \partial \dot{x}_0)$. This yields

$$p_{x_0} = m[x_0] \dot{x}_0. \quad (2.7)$$

Comparing Eqs. (2.5) and (2.7) yields the following alternative expression for the kinetic energy of the solute atoms:

$$T_{UU} = \frac{1}{2} p_{x_0}^T m^{-1}[x_0] p_{x_0}. \quad (2.8)$$

The Hamiltonian of the solution written in generalized coordinates follows immediately from Eqs. (2.1) and (2.8). The result is

$$\begin{aligned} K[p_{x_0}, x_0, p_q, q] \\ = \frac{1}{2} p_{x_0}^T m^{-1}[x_0] p_{x_0} + U_{UU}[x_0] \\ + K_{VV}[p_q, q] + K_{VU}[qx_0], \end{aligned} \quad (2.9)$$

where we have introduced the definitions $U_{UU}[x_0] \equiv U_{UU}[r_0]$, $K_{VV}[p_q, q] \equiv H_{VV}[p_q, q]$, and $K_{VU}[qx_0] = U_{VU}[qr_0]$.

C. Explicit and implicit coordinates

The generalized coordinates x_0 may be partitioned into a set of p explicit coordinates y_0 and a set of $q = 3n - p$ implicit coordinates z_0 ; i.e., we will set

$$x_0 = \begin{pmatrix} y_0 \\ z_0 \end{pmatrix}. \quad (2.10)$$

The explicit coordinates will be constrained to execute small forced oscillations. The implicit coordinates will be permitted to evolve freely in the liquid.

Often we will choose the explicit coordinates to represent displacements from equilibrium of generalized coordinates Y_0 which execute librational motion in the gas phase. Then $y_0 \equiv Y_0 - Y_{0eq}$. For this case, the forced oscillations of the coordinates imposed by the constraints (see Secs. IV and V) closely resemble the vibratory physical motion of the coordinates.

Corresponding to the partitioning of Eq. (2.10), the mass matrix may be partitioned as

$$m[x_0] = \begin{bmatrix} m_{yy}[y_0 z_0] & m_{yz}[y_0 z_0] \\ m_{zy}[y_0 z_0] & m_{zz}[y_0 z_0] \end{bmatrix}, \quad (2.11)$$

where the submatrices $m_{yy}[y_0 z_0]$, etc. are defined by

$$m_{yy}[y_0 z_0] = m_{yy}^T[y_0 z_0] = \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial y_0^T} \right]^T m \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial y_0^T} \right], \quad (2.12a)$$

$$m_{yz}[y_0 z_0] = m_{zy}^T[y_0 z_0] = \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial y_0^T} \right]^T m \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial z_0^T} \right], \quad (2.12b)$$

$$m_{zz}[y_0 z_0] = m_{zz}^T[y_0 z_0] = \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial z_0^T} \right]^T m \left[\frac{\partial \mathbf{r}_0[x_0]}{\partial z_0^T} \right]. \quad (2.12c)$$

The solute kinetic energy may be written in terms of the implicit and explicit generalized coordinates via the relationship

$$\begin{aligned} T_{UU} = \frac{1}{2} [\dot{y}_0^T m_{yy}[y_0 z_0] \dot{y}_0 + \dot{y}_0^T m_{yz}[y_0 z_0] \dot{z}_0 \\ + \dot{z}_0^T m_{zy}[y_0 z_0] \dot{y}_0 + \dot{z}_0^T m_{zz}[y_0 z_0] \dot{z}_0]. \end{aligned} \quad (2.13)$$

The conjugate generalized momenta p_{y_0} and p_{z_0} may be constructed from T_{UU} as

$$p_{y_0} = m_{yy}[y_0 z_0] \dot{y}_0 + m_{yz}[y_0 z_0] \dot{z}_0, \quad (2.14a)$$

$$p_{z_0} = m_{zy}[y_0 z_0] \dot{y}_0 + m_{zz}[y_0 z_0] \dot{z}_0. \quad (2.14b)$$

Comparing Eqs. (2.14) and (2.15) yields the following alternative expression for the kinetic energy T_{UU} :

$$\begin{aligned} T_{UU} = \frac{1}{2} [p_{y_0}^T [m^{-1}[y_0 z_0]]_{yy} p_{y_0} + p_{y_0}^T [m^{-1}[y_0 z_0]]_{yz} p_{z_0} \\ + p_{z_0}^T [m^{-1}[y_0 z_0]]_{zy} p_{y_0} + p_{z_0}^T [m^{-1}[y_0 z_0]]_{zz} p_{z_0}]. \end{aligned} \quad (2.15)$$

The Hamiltonian of the solution written in terms of the generalized coordinates $y_0 z_0$ will be denoted as $K[p_{y_0}, y_0, p_{z_0}, z_0, p_q, q] \equiv K[p_{x_0}, x_0, p_q, q]$. This may be written as

$$\begin{aligned} K[p_{y_0}, y_0, p_{z_0}, z_0, p_q, q] = T_{UU} + U_{UU}[y_0 z_0] + K_{VV}[p_q, q] \\ + K_{VU}[qy_0 z_0], \end{aligned} \quad (2.16)$$

where T_{UU} is given by Eq. (2.15) and where we define $U_{UU}[y_0 z_0] = U_{UU}[x_0]$ and $K_{VU}[qy_0 z_0] = K_{VU}[qx_0]$.

D. Hamilton's equations in generalized coordinates

Because the generalized coordinates $y_0 z_0$ are canonical, the classical equations of motion for these coordinates are of Hamiltonian form. These Hamilton's equations may be written as follows:

$$\dot{p}_{y_0} = F_{gy_0} + \mathcal{F}_{y_0}, \quad (2.17a)$$

$$\dot{y}_0 = \frac{\partial K}{\partial p_{y_0}} = \frac{\partial T_{UU}}{\partial p_{y_0}}, \quad (2.17b)$$

$$\dot{p}_{z_0} = -\frac{\partial K}{\partial z_0} \quad \text{and} \quad \dot{z}_0 = \frac{\partial K}{\partial p_{z_0}}, \quad (2.17c)$$

$$\dot{p}_q = -\frac{\partial K}{\partial q} \quad \text{and} \quad \dot{q} = \frac{\partial K}{\partial p_q}, \quad (2.17d)$$

where we define

$$F_{gy_0} = - \frac{\partial}{\partial y_0} [T_{UU} + U_{UU}[y_0 z_0]] \quad (2.18)$$

and

$$\mathcal{F}_{y_0} = - \frac{\partial K_{VU}[qy_0 z_0]}{\partial y_0} \quad (2.19)$$

The quantities F_{gy_0} and \mathcal{F}_{y_0} are, respectively, the gas phase and solvent generalized forces acting on the coordinates y_0 . Notice that the gas-phase generalized force contains a centripetal-like term arising from the dependence of the kinetic energy T_{UU} on y_0 and z_0 .

E. Liouville operator of the solution

So far our analysis has been purely dynamical. The link to statistical mechanics is provided by the Liouville operator L of the solution. This Liouville operator is defined in terms of the Poisson bracket of the solution $[,]$ in the standard manner as $iL = [, H] = [, K]$. A consequence of the general theory of canonical transformations is that the form and magnitude of the Poisson bracket is invariant under canonical transformation.²³ Given this theorem, one may immediately write down the Liouville operator in generalized coordinates as

$$iL = \sum_{i=1}^p \left\{ \frac{\partial K}{\partial p_{y_{0i}}} \frac{\partial}{\partial y_{0i}} - \frac{\partial K}{\partial y_{0i}} \frac{\partial}{\partial p_{y_{0i}}} \right\} + \sum_{j=1}^q \left\{ \frac{\partial K}{\partial p_{z_{0j}}} \frac{\partial}{\partial z_{0j}} - \frac{\partial K}{\partial z_{0j}} \frac{\partial}{\partial p_{z_{0j}}} \right\} + \sum_{\alpha=1}^s \sum_{\lambda=1}^{N_\alpha} \left\{ \frac{\partial K}{\partial p_{\lambda\alpha}} \frac{\partial}{\partial q_{\lambda\alpha}} - \frac{\partial K}{\partial q_{\lambda\alpha}} \frac{\partial}{\partial p_{\lambda\alpha}} \right\}. \quad (2.22)$$

III. A MODEL GENERALIZED LANGEVIN EQUATION FOR THE COORDINATES y_0

We next develop a model generalized Langevin equation of motion [Eq. (3.1) below] for the dynamics of the coordinates y_0 . In this equation the effects of the solvent force F_{y_0} appearing in the Hamilton equation of motion (2.17a) are simulated by the effects of suitably chosen systematic and random forces.

We expect that the model generalized Langevin equation will realistically simulate the solvent effects on the dynamics of the coordinates y_0 if either: (i) The generalized velocities \dot{y}_0 are small; or (ii) the physical motions of the generalized coordinates in the liquid resemble small ampli-

tude oscillations on molecular time scales.

Condition (ii) holds if the coordinates y_0 are generalized displacements. It will also hold for coordinates y_0 which are not generalized displacements if the motion of the coordinates y_0 is highly hindered at liquid state densities. That is the molecular time scale motion of highly hindered coordinates may be vibratory in the liquid even if the gas phase motion of such coordinates is rotational (as is true for molecular axis rotational coordinates) or aperiodic (as is true for center of mass translational coordinates).

A physical argument for Eq. (3.1) is outlined in Appendix B. This argument gives the following generalized Langevin equation of motion for the generalized momenta p_{y_0} :

$$\begin{aligned} \dot{p}_{y_0}(t) = & F_{gy_0}[p_{y_0}(t)y_0(t), p_{z_0}(t)z_0(t)] + \langle \mathcal{F}_{y_0} \rangle_{y_0(t)} \\ & - [m_{yy}^{1/2}[y_0(t), z_0(t)]] [\omega_{e_0}^2[y_0(t)z_0(t)]] [m_{yy}^{1/2}[y_0(t)z_0(t)]]^T y_0(t) \\ & + \int_0^t d\tau [\omega_{yy}^{1/2}[y_0(t)z_0(t)]] [\omega_{e_0}^2[y_0(t)z_0(t)]] \theta_1[t - \tau; y_0(t)] [\omega_{e_0}^2[y_0(t)z_0(t)]]^T [m_{yy}^{1/2}[y_0(t)z_0(t)]]^T y_0(\tau) \\ & + [m_{yy}^{1/2}[y_0(t)z_0(t)]] [\omega_{e_0}^2[y_0(t)z_0(t)]] [m_{yy}^{1/2}[y_0(t)z_0(t)]]^T R_1[t; y_0(t)]. \end{aligned} \quad (3.1)$$

The gas-phase generalized force F_{gy_0} and the mass matrix element $m_{yy}[y_0 z_0]$ appearing in Eq. (3.1) have been defined earlier in Eqs. (2.18) and (2.12a). The square root of $m_{yy}[y_0 z_0]$ is defined via the Choleski prescription²⁷ for matrix square roots; i.e., via the prescription

$$m_{yy}[y_0 z_0] = m_{yy}^{1/2}[y_0 z_0] [m_{yy}^{1/2}[y_0 z_0]]^T. \quad (3.2)$$

Comparing Eqs. (2.13a) and (3.2) yields the following result for $m_{yy}^{1/2}[y_0 z_0]$:

$$m_{yy}^{1/2}[y_0 z_0] = \left[\frac{\partial r_0[x_0]}{\partial y_0^T} \right]^T m^{1/2}. \quad (3.3)$$

The new quantities appearing in Eq. (3.1) simulate solvent forces acting on the coordinates y_0 . The quantity $\langle \mathcal{F}_{y_0} \rangle_{y_0}$, e.g., is the liquid state contribution to the mean force acting on the coordinates y_0 . This mean force governs static solvent effects on the motion of the y_0 degrees of freedom.

Systematic dynamic solvent effects are governed by the

instantaneous and delayed solvent reaction forces appearing in Eq. (3.1). These are the forces which, respectively, involve the MTGLE quantities $\omega_{e_0}^2[y_0 z_0]$ and $[\omega_{e_0}^2[y_0 z_0]] \theta_1[t; y_0] [\omega_{e_0}^2[y_0 z_0]]^T$. Random dynamic solvent effects are governed by the random force term proportional to the MTGLE quantity $R_1[t; y_0]$.

Molecular expressions for the MTGLE quantities appearing in Eq. (3.1) are given in Sec. V E. These expressions permit one to rigorously calculate the quantities from MD simulations of the motion of the $z_0 q$ degrees of freedom conditional that the explicit coordinates are clamped at y_0 .

IV. CONSTRAINED DYNAMICS

The linear response of the implicit and solvent degrees of freedom to small forced oscillations of the explicit coordinates will be considered in Sec. V. A proper treatment of this linear response requires one to consider the problem of classical mechanics in the presence of constraints. This problem

is treated in standard textbooks.²³

Using the results of this treatment one finds the Hamilton equations of motion of the liquid solution, given that the explicit degrees of freedom are constrained to execute small forced oscillations, are

$$\dot{p}_{y_0j}(t) = -\frac{\partial K}{\partial y_{0j}(t)} + \lambda_j(t), \quad (4.1a)$$

$$\dot{y}_{0j}(t) = \frac{\partial K}{\partial p_{y_0j}(t)}, \quad j = 1, 2, \dots, p, \quad (4.1b)$$

$$\dot{p}_{z_0}(t) = -\frac{\partial K}{\partial z_0(t)} \quad \text{and} \quad \dot{z}_0(t) = \frac{\partial K}{\partial p_{z_0}(t)}, \quad (4.2)$$

$$\dot{p}_q(t) = -\frac{\partial K}{\partial q(t)} \quad \text{and} \quad \dot{q}(t) = \frac{\partial K}{\partial p_q(t)}. \quad (4.3)$$

The $\lambda_j(t)$ are undetermined Lagrange multipliers which account for the effects of constraints for the case of small forced oscillations.

We close this Section by introducing some short-hand notation we will often use in the remainder of the paper. We will often denote the phase space coordinates of the solvent and implicit solute degrees of freedom collectively by Q , i.e.,

$$Q \equiv (p_{z_0}, z_0, p_q, q). \quad (4.4)$$

Correspondingly the phase space volume element of these degrees of freedom will be denoted by dQ where

$$dQ \equiv dp_{z_0} dz_0 dp_q dq. \quad (4.5)$$

V. LINEAR RESPONSE MODEL FOR THE y_0 -DEPENDENT CORRELATION FUNCTIONS

We next develop molecular expressions for the MTGLE matrices $\omega_{e_0}^2 [y_0 z_0]$ etc. appearing in the generalized Langevin equation (3.1).

The idea behind this development is as follows: One subjects the explicit coordinates to small forced displacements $\Delta y_0(t)$ about point y_0 . One then calculates the linear

order reaction force exerted by the *solvent* on the explicit coordinates. Molecular expressions for the MITGLE matrices may then be obtained by comparing this reaction force with Eq. (3.1).

Our calculation is a generalization of one presented elsewhere.²⁸ Thus the discussion here will be restricted to an outline which will emphasize the new features not required in the earlier treatment.

To carry out the linear response treatment one must determine the phase space probability distribution function $(pdf)f[Q;t]$ of the solvent and the implicit solute degrees of freedom to order $\Delta y_0(t)$.

The time dependence of $f[Q;t]$ is governed by a Liouville operator L_c which described dynamics in the constrained solution. To order $\Delta y_0(t)$ L_c may be expressed in terms of the Hamiltonian K_0 of the solution conditional that the explicit coordinate are fixed at y_0 . We next derive K_0 .

A. The Hamiltonian K_0

The Hamiltonian K_0 is [cf. Eq. (2.16)]

$$\begin{aligned} K_0 &= K_0[Q; y_0] \\ &= T_{UU}^0 + U_{UU}[y_0 z_0] + K_{VV}[p_q q] + K_{VV}[q y_0 z_0], \end{aligned} \quad (5.1)$$

where T_{UU}^0 is the kinetic energy of the solute molecule given that the explicit coordinates are fixed at $y_0 = 0$. Using Eq. (2.13) yields

$$T_{UU}^0 = \frac{1}{2} \dot{z}_0 m_{zz} [y_0 z_0] \dot{z}_0. \quad (5.2)$$

The generalized momenta p_{z_0} for the case $\dot{y}_0 = 0$ follow from Eq. (2.14b) as

$$p_{z_0} = m_{zz} [y_0 z_0] \dot{z}_0. \quad (5.3)$$

Comparing Eqs. (5.2) and (5.3) yields the following alternative form for T_{UU}^0 :

$$T_{UU}^0 = \frac{1}{2} p_{z_0} m_{zz}^{-1} [y_0 z_0] p_{z_0}. \quad (5.4)$$

B. The Liouville operator L_c

The form of the Liouville operator L_c may be rigorously derived²⁹ from the constrained equations of motion (4.2) and (4.3). In Appendix B we present a simplified heuristic argument which gives L_c correct to order $\Delta y_0(t)$. [This is sufficient to determine $f[Q;t]$ to order $\Delta y_0(t)$]. The result for L_c is

$$L_c = L_0 + L^{(1)}(t), \quad (5.5)$$

where [cf. Eq. (2.22)]

$$iL_0 = \sum_{\alpha=1}^g \left\{ \frac{\partial K_0}{\partial p_{x_0\alpha}} \frac{\partial}{\partial z_{0\alpha}} - \frac{\partial K_0}{\partial z_{0\alpha}} \frac{\partial}{\partial p_{x_0\alpha}} \right\} + \sum_{\alpha=1}^s \sum_{\lambda=1}^{N_\alpha} \left\{ \frac{\partial K_0}{\partial p_{\lambda\alpha}} \frac{\partial}{\partial p_{\lambda\alpha}} - \frac{\partial K_0}{\partial q_{\lambda\alpha}} \frac{\partial}{\partial p_{\lambda\alpha}} \right\} \quad (5.6)$$

and where

$$iL^{(1)}(t) = \left[\sum_{\alpha=1}^g \left\{ \frac{\partial}{\partial p_{x_0\alpha}} \frac{\partial F_{0y_0}^T}{\partial z_{0\alpha}} - \frac{\partial}{\partial z_{0\alpha}} \frac{\partial F_{0y_0}^T}{\partial p_{x_0\alpha}} \right\} + \sum_{\alpha=1}^s \sum_{\lambda=1}^{\alpha} \left\{ \frac{\partial}{\partial p_{\lambda\alpha}} \frac{\partial F_{0y_0}^T}{\partial q_{\lambda\alpha}} - \frac{\partial}{\partial q_{\lambda\alpha}} \frac{\partial F_{0y_0}^T}{\partial p_{\lambda\alpha}} \right\} \right] \cdot \Delta y_0(t). \quad (5.7)$$

The generalized for F_{0y_0} appearing in Eq. (5.7) is defined by

$$F_{0y_0} = -\frac{\partial K_0}{\partial y_0}. \quad (5.8)$$

Notice that to order $\Delta y_0(t)$, L_c is independent of the still undetermined Lagrange multipliers λ_j .

C. Canonical ensemble averages in the constrained solution

The MTGLE quantities are defined as canonical ensemble averages conditional that the explicit coordinates are fixed at y_0 . Such canonical averages, which will be denoted by the symbol $\langle \rangle_{y_0}$, are defined for an arbitrary dynamical variable $A = A[Q; y_0]$ by

$$\langle A \rangle_{y_0} = \int f_{\text{CA}}^{(0)}[Q; y_0] A[Q; y_0] dQ. \quad (5.9)$$

The quantity $f_{\text{CA}}^{(0)}[Q; y_0]$ is the canonical ensemble probability distribution function (pdf) conditional that the explicit coordinates are clamped at y_0 and is thus given by $[\beta \equiv (k_B T)^{-1}]$

$$f_{\text{CA}}^{(0)}[Q; y_0] = [Z_{\text{CA}}^{(0)}[y_0]]^{-1} \exp[-\beta K_0[Q; y_0]], \quad (5.10)$$

where K_0 is defined in Eq. (5.4) and where the partition function $Z_{\text{CA}}^{(0)}[y_0]$ is defined by

$$Z_{\text{CA}}^{(0)}[y_0] \equiv \int \exp[-\beta K_0] dQ. \quad (5.11)$$

D. Linear response model for the solvent force

We next outline the linear response calculation of the MTGLE matrices. These may be obtained by comparing the total generalized force $F_{y_0}(t)$ exerted on the explicit coordinates at time t with Eq. (3.1). This total force may be decomposed into a gas-phase force $F_{g y_0}(t)$ and a solvent force. The solvent force may be further decomposed into a systematic component $\langle \mathcal{F}_{y_0} \rangle_t$ defined by

$$\langle \mathcal{F}_{y_0} \rangle_t = \int f[Q; t] \mathcal{F}_{y_0}[q y_0 + \Delta y_0(t) z_0] dQ \quad (5.12)$$

and a random component $\tilde{\mathcal{F}}_{y_0}[t; y_0]$ defined by

$$\tilde{\mathcal{F}}_{y_0}[t; y_0] = \mathcal{F}_{y_0}[t; y_0] - \langle \mathcal{F}_{y_0} \rangle_{y_0}, \quad (5.13)$$

where $\mathcal{F}_{y_0}[t; y_0] = \exp[iL_0 t] \mathcal{F}_{y_0}$ with \mathcal{F}_{y_0} defined in Eq. (2.19).

Equation (5.12) and the linear response result²⁸ for $f[Q; t]$ yields the following result for $\langle \mathcal{F}_{y_0} \rangle_t$ to order $\Delta y_0(t)$:

$$\begin{aligned} \omega_{e_0}^2[y_0 z_0] &= [\omega_{e_0}^2[y_0 z_0]]^T \\ &= -[m_{yy}^{-1/2}[y_0 z_0]] \left[\left\langle \frac{\partial \mathcal{F}_{y_0}}{\partial y_0^T} \right\rangle_{y_0} \right] [m_{yy}^{-1/2}[y_0 z_0]]^T, \end{aligned} \quad (5.18a)$$

$$\begin{aligned} \dot{\theta}_1[t; y_0] &= \dot{\theta}^T[t; y_0] \\ &= \beta [\omega_{e_1}^{-2}[y_0 z_0]] [m_{yy}^{-1/2}[y_0 z_0]] \langle \tilde{\mathcal{F}}_{y_0}[t; y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0} [m_{yy}^{-1/2}[y_0 z_0]]^T [\omega_{e_1}^{-2}[y_0 z_0]]^T, \end{aligned} \quad (5.18b)$$

$$[m_{yy}^{1/2}[y_0 z_0]] \omega_{e_1}^2[y_0 z_0] [m_{yy}^{1/2}[y_0 z_0]]^T R_1[t; y_0] = \tilde{\mathcal{F}}_{y_0}[t; y_0]. \quad (5.18c)$$

Following our earlier work¹ we will normalize the response function so that $\dot{\theta}[t; r_0] = 1$. Given this normalization, the molecular expression for the MTGLE parameter $\omega_{e_1}^4[y_0 z_0] = [\omega_{e_1}^2[y_0 z_0]] [\omega_{e_1}^2[y_0 z_0]]^T$ follows by setting $t = 0$ in Eq. (5.18b). The result is

$$\omega_{e_1}^4[y_0 z_0] = [\omega_{e_1}^4[y_0 z_0]]^T = \beta [m_{yy}^{-1/2}[y_0 z_0]] \langle \tilde{\mathcal{F}}_{y_0}[y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0} [m_{yy}^{-1/2}[y_0 z_0]]^T. \quad (5.18d)$$

Comparison of Eqs. (5.18c) and (5.18d), moreover, yields the following second fluctuation-dissipation theorem:

$$\dot{\theta}_1[t; y_0] = \beta \langle iL_0 [m_{yy}^{1/2}[y_0 z_0]]^T [R_1[t; y_0]] iL_0 [m_{yy}^{1/2}[y_0 z_0]] R_1^T[t; y_0] \rangle_{y_0}. \quad (5.19)$$

$$\begin{aligned} \langle F_{y_0} \rangle_t &= \langle F_{y_0} \rangle_{y_0} + \left\langle \frac{\partial \mathcal{F}_{y_0}}{\partial y_0^T} \right\rangle_{y_0} \cdot \Delta y_0(t) \\ &+ \beta \int_0^t \langle \tilde{\mathcal{F}}_{y_0}[t - \tau; y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0} \cdot \Delta y_0(\tau) d\tau \end{aligned} \quad (5.14)$$

with

$$\tilde{\mathcal{F}}_{y_0}[y_0] = iL_0 [F_{y_0} - \langle \mathcal{F}_{y_0} \rangle_{y_0}]. \quad (5.15)$$

For many important choices of generalized coordinates³⁰ the following relationship holds exactly or approximately:

$$\langle \tilde{\mathcal{F}}_{y_0}[t; y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0} = \langle \tilde{\mathcal{F}}_{y_0}[t; y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0}. \quad (5.16)$$

The physical meaning of Eq. (5.23) is as follows: The y_0 and z_0 coordinates are coupled by both the gas-phase Hamiltonian and also the solute-solvent potential. Because of this coupling, motion of the z_0 coordinates is induced by the displacements $\Delta y_0(t)$. This induced z_0 motion causes solvent relaxation. This relaxation, in turn, gives rise to the delayed solvent force exerted on the y_0 coordinates. Equation (5.23) amounts to neglecting the contribution to the delayed force due to that part of the z_0 motion induced by the *gas-phase* y_0 , z_0 coupling.

We will restrict our analysis in the remainder of this paper to cases for which Eq. (5.16) holds exactly or approximately.

Assuming Eq. (5.16) holds the total generalized for $F_{y_0}(t)$ may be written as

$$\begin{aligned} F_{y_0}(t) &= F_{g y_0}(t) + \langle \mathcal{F}_{y_0} \rangle_{y_0} + \left\langle \frac{\partial \mathcal{F}_{y_0}}{\partial y_0^T} \right\rangle_{y_0} \cdot \Delta y_0(t) \\ &+ \beta \int_0^t \langle \tilde{\mathcal{F}}_{y_0}[t - \tau; y_0] \tilde{\mathcal{F}}_{y_0}^T[y_0] \rangle_{y_0} \cdot \Delta y_0(\tau) d\tau + \tilde{F}_{y_0}[t; y_0]. \end{aligned} \quad (5.17)$$

E. Molecular expressions for the MTGLE matrices

Equations (3.1) and (5.17) are identical to linear order in $\Delta y_0(t)$ if one makes the identification $y_0(t) \rightarrow \Delta y_0(t)$ at appropriate points in Eq. (3.1). (The justification for this identification is discussed in Appendix A.) Comparison of Eqs. (3.1) and (5.22) then yields the following molecular expressions for the MTGLE matrices:

VI. SEPARATION OF THE EFFECTS OF FLUCTUATIONS IN THE z_0 AND q DEGREES OF FREEDOM

The molecular expressions [Eqs. (5.18)] just derived provide a useful prescription for computation of the MTGLE matrices. They do not, however, permit one to easily separate the contributions of the z_0 and q fluctuations to the overall solvent influence on y_0 coordinate motion. We next present a prescription which permits one to separate these contributions as far as is apparently possible.

This separation can lead to better understanding of the mechanism of energy exchange between the explicit and solvent coordinates. Suppose, e.g., that if z_0 fluctuations are suppressed the frequency spectra of the y_0 degrees of freedom and the solvent do not appreciably overlap. Suppose, however, overlap occurs when the z_0 fluctuations are reinstated. Then one expects the indirect energy transfer process $y_0 \rightarrow z_0 \rightarrow q$ to occur at a faster rate than the direct process $y_0 \rightarrow q$.

A. Factorization of $f_{CA}^{(0)}[Q; y_0]$

The separation of the effects of the z_0 and q motions just mentioned is based on the following rigorous factorization of the canonical ensemble distribution function $f_{CA}^{(0)}[Q; y_0]$ derived in Appendix C:

$$f_{CA}^{(0)}[Q; y_0] = f_{CA}^{(0)}[p_{z_0}; y_0] f_{CA}^{(0)}[p_q q; y_0 z_0]. \quad (6.1)$$

The probability distribution functions (pdf) appearing on the right-hand side of Eq. (6.1) are as follows. The pdf $f_{CA}^{(0)}[p_q q; y_0 z_0]$ is the canonical ensemble distribution function of the solvent conditional that the solute is *fully clamped* at configuration point $r_0 = y_0 z_0$. This pdf is defined in terms of the solvent-solvent $K_{VV}[p_q q]$ and solvent-solute $K_{VU}[q y_0 z_0]$ potential energy functions via

$$f_{CA}^{(0)}[p_q q; y_0 z_0] = [Z_{CA}^{(0)}[y_0 z_0]]^{-1} \times \exp[-\beta(K_{VV}[p_q q] + K_{VU}[q y_0 z_0])], \quad (6.2)$$

where

$$Z_{CA}^{(0)}[y_0 z_0] = \int dp_q dq \times \exp[-\beta(K_{VV}[p_q q] + K_{VU}[q y_0 z_0])] \quad (6.3)$$

is the partition function of the solvent given that the solute is clamped at configuration point $r_0 = y_0 z_0$.

The pdf $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$ is the probability distribution function for the phase space coordinates $p_{z_0} z_0$, in the *liquid solution*, conditional that the explicit coordinates are fixed at y_0 . This is defined by

$$f_{CA}^{(0)}[p_{z_0} z_0; y_0] = [Z_{CA}^{(0)}[y_0]]^{-1} \times \exp[-\beta(\frac{1}{2} p_{z_0}^T m_{zz}^{-1} [y_0 z_0] p_{z_0} + W_{UU}[y_0 z_0])]. \quad (6.4)$$

The quantity $W_{UU}[y_0 z_0]$ is the potential of mean force acting on the solute system when it is located at configuration point $r_0 = y_0 z_0$. This potential of mean force is the sum of the gas-phase solute potential energy function $U_{UU}[y_0 z_0]$ and a liquid state correction, the solute cavity potential

$w_{UU}[y_0 z_0]$, i.e.,

$$W_{UU}[y_0 z_0] = U_{UU}[y_0 z_0] + w_{UU}[y_0 z_0]. \quad (6.5)$$

The pdf $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$ is unit normalized [see Eq. (B3)]. Thus the partition function $Z_{CA}^{(0)}[y_0]$, defined as a many-body configurational integral in Eq. (5.11), may alternatively be written as the following solute molecule configurational integral:

$$Z_{CA}^{(0)}[y_0] = \int dp_{z_0} dz_0 \times \exp[-\beta(\frac{1}{2} p_{z_0}^T m_{zz}^{-1} [y_0 z_0] p_{z_0} + W_{UU}[y_0 z_0])]. \quad (6.6a)$$

Using the result

$$\int dp_{z_0} \exp\left[-\frac{\beta}{2} (p_{z_0}^T m_{zz}^{-1} [y_0 z_0] p_{z_0})\right] = \left(\frac{2\pi}{\beta}\right)^{q/2} \left\{ \det[m_{zz}[y_0 z_0]] \right\}^{1/2}, \quad (6.7)$$

we have that $Z_{CA}^{(0)}[y_0]$ may be rewritten as

$$Z_{CA}^{(0)}[y_0] = \left(\frac{2\pi}{\beta}\right)^{q/2} \int dz_0 \{ \det[m_{zz}(y_0 z_0)] \}^{1/2} \times \exp[-\beta W_{UU}[y_0 z_0]]. \quad (6.6b)$$

The advantage of the rigorous factorization given in Eq. (6.1) is that averages $\langle A \rangle_{y_0}$ of dynamical variables $A[Q; y_0] \equiv A$ may be performed in two steps. Namely:

(i) The average of A over solvent phase space coordinates is performed using the distribution function $f_{CA}^{(0)}[p_q q; y_0 z_0]$ to yield the average $\langle A \rangle_{y_0 p_{z_0} z_0}$ defined by

$$\langle A \rangle_{y_0 p_{z_0} z_0} = \int f_{CA}^{(0)}[p_q q; y_0 z_0] A[Q; y_0] dp_q dq.$$

(If A is independent of p_{z_0} we will denote $\langle A \rangle_{y_0 p_{z_0} z_0}$ by $\langle A \rangle_{y_0 z_0}$.) This average includes contributions from fluctuations in the solvent coordinates but not from fluctuations in the coordinates z_0 .

(ii) The average of $\langle A \rangle_{y_0 p_{z_0} z_0}$ over the phase space coordinates $p_{z_0} z_0$ is performed using the pdf $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$ to yield $\langle A \rangle_{y_0}$, i.e.,

$$\langle A \rangle_{y_0} = \int f_{CA}^{(0)}[p_{z_0} z_0; y_0] \langle A \rangle_{y_0 p_{z_0} z_0} dp_{z_0} dz_0.$$

Since $\langle A \rangle_{y_0}$ contains contributions from both z_0 and q fluctuations, numerical comparison of $\langle A \rangle_{y_0}$ and $\langle A \rangle_{y_0 p_{z_0} z_0}$ permits one to separate the effects of the fluctuations on the magnitude of $\langle A \rangle_{y_0}$.

An example of this procedure consider the calculation of the liquid state contribution to the generalized mean force $\langle \mathcal{F}_{y_0} \rangle_{y_0}$. One first calculates the quantity $\langle \mathcal{F}_{y_0} \rangle_{y_0 p_{z_0} z_0} = \langle \mathcal{F} \rangle_{y_0 z_0}$ defined by

$$\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0} = \int f_{CA}^{(0)}[p_q q; y_0 z_0] \mathcal{F}_{y_0}[q y_0 z_0] dp_q dq. \quad (6.8a)$$

Then $\langle \mathcal{F}_{y_0} \rangle_{y_0}$ may be calculated via the relationship

$$\langle \mathcal{F}_{y_0} \rangle_{y_0} = \int dp_{z_0} dz_0 f_{CA}^{(0)}[p_{z_0} z_0; y_0] \langle \mathcal{F}_{y_0} \rangle_{y_0 z_0}. \quad (6.9)$$

For the present case, the calculation may be simplified by using the following relationship between $\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0}$ and the solute cavity potential:

$$\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0} = - \frac{\partial w_{UU} [y_0 z_0]}{\partial y_0}. \quad (6.8b)$$

B. Separation of the effects of fluctuations for $\omega_{e_0}^2 [y_0 z_0]$ and $\omega_{c_1}^4 [y_0 z_0]$.

We next develop expressions for $\omega_{e_0}^2 [y_0 z_0]$ and $\omega_{c_1}^4 [y_0 z_0]$ which permit one to separate the effects of fluctuations.

Using the procedure just outlined, $\omega_{e_0}^2 [y_0 z_0]$ may be calculated from Eq. (5.24a) to yield

$$[m_{yy}^{1/2} [y_0 z_0]] \omega_{e_0}^2 [y_0 z_0] [m_{yy}^{1/2} [y_0 z_0]]^T = \int dp_{z_0} dz_0 f_{CA}^{(0)} [p_{z_0} z_0 | y_0] \left[\left\langle \frac{\partial^2 K_{VU}}{\partial y_0 \partial y_0^T} \right\rangle_{y_0 z_0} \right]. \quad (6.10a)$$

Since $\langle \partial^2 K_{VU} / \partial y_0 \partial y_0^T \rangle_{y_0 z_0}$ is independent of p_{z_0} , the integral over p_{z_0} in Eq. (6.10a) may be performed analytically to yield

$$[m_{yy}^{1/2} [y_0 z_0]] \omega_{e_0}^2 [y_0 z_0] [m_{yy}^{1/2} [y_0 z_0]]^T = \left(\frac{2\pi}{\beta} \right)^{q/2} [Z_{CA}^{(0)} [y_0]]^{-1} \times \int dz_0 \{ \det [m_{zz} [y_0 z_0]] \}^{1/2} \exp [- \beta W_{UU} [y_0 z_0]] \left[\left\langle \frac{\partial^2 K_{VU}}{\partial y_0 \partial y_0^T} \right\rangle_{y_0 z_0} \right]. \quad (6.10b)$$

We next give an analogous expression for $\omega_{c_1}^4 [y_0 z_0]$ based on Eq. (5.24d). A calculation yields

$$[m_{yy}^{1/2} [y_0 z_0]] \omega_{c_1}^4 [y_0 z_0] [m_{yy}^{1/2} [y_0 z_0]]^T = \left(\frac{2\pi}{\beta} \right)^{q/2} [Z_{CA}^{(0)} [y_0]]^{-1} \int dz_0 \{ \det [m_{zz} [y_0 z_0]] \}^{1/2} \exp [- \beta W_{UU} [y_0 z_0]] \times \left[\beta \langle \mathcal{F}_{y_0}^{(0)} [y_0] \mathcal{F}_{y_0}^{(0)T} [y_0] \rangle_{y_0 z_0} + \sum_{i=1}^q \sum_{j=1}^q \left\langle \frac{\partial \mathcal{F}_{y_0} [y_0]}{\partial z_{0i}} \frac{\partial \mathcal{F}_{y_0}^T [y_0]}{\partial z_{0j}} \right\rangle_{y_0 z_0} [m_{zz}^{-1} [y_0 z_0]]_{ij} \right], \quad (6.11)$$

where $\mathcal{F}_{y_0} [y_0] = iL_{0q} F_{y_0} [y_0]$ and where

$$iL_{0q} = \sum_{\alpha=1}^s \sum_{\lambda=1}^{N_\alpha} \left\{ \frac{\partial K_0}{\partial \mathbf{p}_{\lambda\alpha}} \cdot \frac{\partial}{\partial \mathbf{q}_{\lambda\alpha}} - \frac{\partial K_0}{\partial \mathbf{q}_{\lambda\alpha}} \cdot \frac{\partial}{\partial \mathbf{p}_{\lambda\alpha}} \right\} \quad (6.12)$$

is the Liouville operator of the solvent given that the solute is fully clamped.

C. Separation of the effects of fluctuations for the response function

We next discuss the separation of fluctuations for the response function defined in Eq. (5.24b). It is actually more convenient to discuss the friction kernel $\beta_1 [t; y_0]$ which is proportional to the time integral of $\theta_1 [t; y_0]$. The friction kernel is defined by

$$\beta_1 [t; y_0] = \beta \langle \mathcal{F}_{0y_0} [t; y_0] \mathcal{F}_{0y_0}^T [y_0] \rangle_{y_0}. \quad (6.13a)$$

The friction kernel $\beta_1 [t; y_0]$ provides a direct measure of how coupled z_0 and q fluctuations influence the energy flow from the y_0 modes. The quantity $\beta_1^{(0)} [t; y_0]$ defined by

$$\begin{aligned} \beta_1^{(0)} [t; y_0] &= \beta \langle \mathcal{F}_{y_0}^{(0)} [t; y_0] \mathcal{F}_{y_0}^{(0)T} [y_0] \rangle_{y_0 z_0} \\ &\equiv \beta \langle \exp [iL_{0q} t] \mathcal{F}_{y_0} [y_0] \mathcal{F}_{y_0}^T [y_0] \rangle_{y_0 z_0}, \end{aligned} \quad (6.13b)$$

in contrast, provides a direct measure of how pure q fluctuations influence the energy dissipation. Thus a numerical comparison of $\beta_1 [t; y_0]$ and $\beta_1^{(0)} [t; y_0 z_0]$, or preferably the frequency spectra of these quantities, should provide insight into the microscopic details of the local energy disposal.

VII. SUMMARY

This paper presents an analysis of the classical dynamics of an n -atom solute system immersed at infinite dilution in a monatomic solvent. The analysis is designed to aid in the interpretation of solvent effects on spectroscopic, energy

transfer, and chemical reaction processes involving the solute system. The theoretical treatment is based on a synthesis of recently developed generalized Langevin equation techniques¹ with the methods of classical mechanics.²³

The main results of the theory developed in this paper are:

- (i) The generalized Langevin equation of motion [Eq. (3.1)] for the p explicit solute coordinates whose dynamics governs the kinetic or spectroscopic process of interest;
- (ii) The molecular formulas (5.18) and (6.8b) for the liquid state quantities appearing in the generalized Langevin equation;
- (iii) The approximate second fluctuation-dissipation theorem [Eq. (5.19)];
- (iv) The rigorous method for assessing the relative contributions of solvent and implicit coordinate fluctuations to the generalized mean force acting in the explicit coordinates [Eqs. (6.8) and (6.9)]; the MTGLE parameters, Eqs. (6.10) and (6.11); the friction kernel [Eq. (6.13)]; and hence the solvation shell fluctuation spectrum.

The generalized Langevin equation of motion, while approximate, is expected to realistically describe explicit coordinate dynamics if:

- (i) The explicit coordinates are generalized displacements and hence execute oscillatory motion in both the gas and liquid phases;
- (ii) The liquid state motion of the explicit coordinates is

sufficiently hindered by cage effects that it is oscillatory on subpicosecond time scales even if it is diffusive on longer time scales;

(iii) The generalized velocities \dot{y}_0 are small.

The approximate second fluctuation-dissipation theorem holds if the influence of *gas-phase* couplings between the implicit and explicit coordinates on the solvent fluctuation spectrum are ignored.

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APPENDIX A: PHYSICAL ARGUMENT FOR THE GENERALIZED LANGEVIN EQUATION [EQ. (3.1)]

We next present a physical argument for the model generalized Langevin equation of motion [Eq. (3.1)]. For simplicity of presentation, we develop Eq. (3.1) for the case that the coordinates y_0 represent generalized displacements, i.e., $y_0(t) = Y_0(t) - Y_{0eq}$. We have mentioned in Sec. III that Eq. (3.1) is a valid model equation of motion for coordinates y_0 which are not generalized displacements if either:

(i) The generalized velocities are sufficiently small that the dissipative solvent forces acting on the generalized coordinates y_0 may be taken as linear functionals of the generalized velocities \dot{y}_0 ;

(ii) The liquid state motion of the generalized coordinates resembles that of generalized displacements on a picosecond timescale even though it may be diffusive on a longer time scale.

We assume that the generalized displacements $y_0(t)$ are initially fixed by a constraint force to remain at point $y_0(0)$ for $t < 0$. That is $y_0(t) = y_0(0)$ for $t < 0$. Then, excluding the constraint force, the generalized force $F_{y_0}[t; y_0]$ acting on the coordinates y_0 for $t < 0$ is

$$F_{y_0}[t; y_0(0)] = F_{g_0}[p_{y_0}(t)y_0(0), p_{z_0}(t)z_0(t)] + \mathcal{F}_{y_0}[q(t)z_0(t)|y_0(0)], \quad (A1)$$

where the gas-phase and solvent forces are defined in Eqs. (2.18) and (2.19).

We may rewrite Eq. (A1) as a sum of systematic and random forces. Explicitly

$$F_{y_0}[t; y_0(0)] = F_{g_0}[p_{y_0}(t)y_0(0), p_{z_0}(t)z_0(t)] + \langle \mathcal{F}_{y_0} \rangle_{y_0} + \tilde{\mathcal{F}}_{0y_0}[t; y_0(0)], \quad (A2)$$

where

$$\tilde{\mathcal{F}}_{0y_0}[t; y_0] \equiv \mathcal{F}_{y_0}[q(t)z_0(t)|y_0] - \langle \mathcal{F}_{y_0} \rangle_{y_0} \quad (A3)$$

is the fluctuating solvent force exerted on the fixed coordinates y_0 .

Next assume that at $t = 0$ the constraint force is removed. Thus for $t > 0$ the coordinates y_0 execute their natural motion in the solvent. Since these coordinates are generalized displacements, this natural or "free" motion consists of oscillations $y_0(t)$ about $y_0 = 0$.

Denote the average (over the z_0q phase space coordinates) solvent force exerted on the freely moving coordinates y_0 by $\langle \mathcal{F}_{y_0} \rangle_t$. This force may be written as a superposition of the initial solvent force $\langle \mathcal{F}_{y_0} \rangle_{y_0(0)}$ and a correction due to the deviation $\Delta y_0(t) = y_0(t) - y_0(0)$ of the displacements $y_0(t)$ from their initial values $y_0(0)$. This correction force, is, in general, a functional of $y_0(t)$ which must vanish if $\Delta y_0(t) = 0$. For small amplitude oscillations $y_0(t)$, this correction force may be realistically approximated by a linear functional of $y_0(t)$.

The most general form for $\langle \mathcal{F}_{y_0} \rangle_t$, valid for small amplitude oscillations, which meets these criteria is

$$\langle \mathcal{F}_{y_0} \rangle_t = \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} + \int_0^t \Phi[t - \tau; y_0 = 0] \Delta y_0(\tau) d\tau, \quad (A4)$$

where $\Phi[t; y_0 = 0]$ is a still undetermined linear response function which governs the average reaction force exerted by the solvent on the freely moving coordinates as they oscillate about the equilibrium point $y_0 = 0$.

We next replace $\Phi[t - \tau; y_0 = 0]$ by $\Phi[t - \tau; y_0(t)]$ in Eq. (A4). This yields

$$\langle \mathcal{F}_{y_0} \rangle_t = \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} + \int_0^t \Phi[t - \tau; y_0(t)] \Delta y_0(\tau) d\tau. \quad (A5)$$

The justification for the replacement $\Phi[t - \tau; y_0 = 0] \rightarrow \Phi[t - \tau; y_0(t)]$ is that Eqs. (A4) and (A5) are identical to the linear order in $y_0(t)$ for which Eq. (A4) is valid.

The linear response function $\Phi[t; y_0]$ may, in general, be decomposed into instantaneous $\Phi_i[y_0]$ and delayed $\Phi_d[t; y_0]$ components; i.e.,

$$\Phi[t; y_0] = 2\Phi_i[y_0]\delta(t) + \Phi_d[t; y_0]. \quad (A6)$$

Combining Eqs. (A5) and (A6) yields the following result for $\langle \mathcal{F}_{y_0} \rangle_t$:

$$\langle \mathcal{F}_{y_0} \rangle_t = \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} + \Phi_i[y_0(t)] \Delta y_0(t) + \int_0^t \Phi_d[t - \tau; y_0(t)] \Delta y_0(\tau) d\tau, t > 0. \quad (A7)$$

Equation (A7) gives the *average* solvent force exerted on the freely moving coordinates y_0 at time t . The actual solvent force exerted on these coordinates at time t is $\mathcal{F}_{y_0}[q(t)z_0(t)|y_0(t)]$. The actual solvent force may be rewritten as a sum of systematic, i.e., average and random forces via the relation

$$\mathcal{F}_{y_0}[q(t)z_0(t)|y_0(t)] = \langle \mathcal{F}_{y_0} \rangle_t + \tilde{\mathcal{F}}_{y_0}[t; y_0(t)], \quad (A8)$$

where the random force $\tilde{\mathcal{F}}_{y_0}[t; y_0(t)]$ is defined by

$$\tilde{\mathcal{F}}_{y_0}[t; y_0(t)] \equiv \mathcal{F}_{y_0}[q(t)z_0(t)|y_0(t)] - \langle \mathcal{F}_{y_0} \rangle_t. \quad (A9)$$

To obtain the total force $F_{y_0}[t; y_0(t)]$ acting on the coordinates y_0 at time t one must add the instantaneous gas phase force to eq. (A8). This yields the following expression for $F_{y_0}[t; y_0(t)]$:

$$F_{y_0}[t; y_0(t)] = F_{g_0}[p_{y_0}(t)y_0(t), p_{z_0}(t)z_0(t)] + \langle \mathcal{F}_{y_0} \rangle_t + \tilde{\mathcal{F}}_{y_0}[t; y_0(t)]. \quad (A10)$$

We next define the MTGLE quantities $\omega_c^2[y_0z_0]$, $\omega_c^2[y_0z_0]$, and $\theta_1[t; y_0]$ in terms of the instantaneous and delayed solvent response functions via the relations

$$[m_{yy}^{1/2}[y_0 z_0]] [\omega_c^2[y_0 z_0] - \Omega_0^2[y_0 z_0]] [m_{yy}^{1/2}[y_0 z_0]]^T = -\Phi_i[y_0], \quad (\text{A11})$$

$$[m_{yy}^{1/2}[y_0 z_0]] [\omega_c^4[y_0 z_0]] [m_{yy}^{1/2}[y_0 z_0]]^T = \dot{\Phi}_d[t=0; y_0], \quad (\text{A12})$$

$$[m_{yy}^{1/2}[y_0 z_0]] [\omega_c^2[y_0 z_0]] \theta_1[t; y_0] [\omega_c^2[y_0 z_0]]^T \times [m_{yy}^{1/2}[y_0 z_0]]^T = \Phi_d[t; y_0], \quad (\text{A13})$$

where the squared adiabatic frequency matrix $\Omega_0^2[y_0 z_0]$ is defined by

$$\Omega_0^2[y_0 z_0] = -[m_{yy}^{-1/2}[y_0 z_0]] \times \left[\frac{\partial \langle \mathcal{F}_{y_0} \rangle_{y_0}}{\partial y_0^T} \right] [m_{yy}^{-1/2}[y_0 z_0]]^T. \quad (\text{A14})$$

The MTGLE random force may similarly be defined in terms of $\mathcal{F}_{y_0}[t; y_0(t)]$ by

$$[m_{yy}^{1/2}[y_0(t) z_0(t)]] [\omega_c^2[y_0(t) z_0(t)]] [m_{yy}^{1/2}[y_0(t) z_0(t)]]^T R_1[t; y_0(t)] = \mathcal{F}_{y_0}[t; y_0(t)]. \quad (\text{A15})$$

Combining the above results yields the following equation of motion for the generalized momenta p_{y_0} {recall $\dot{p}_{y_0}(t) = F_{y_0}[t; y_0(t)]$ }:

$$\begin{aligned} \dot{p}_{y_0}(t) = & F_{g_{y_0}}[p_{y_0}(t) y_0(t), p_{z_0}(t) z_0(t)] + \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} - [m_{yy}^{1/2}[y_0(t) z_0(t)]] \\ & \times [\omega_c^2[y_0(t) z_0(t)] - \Omega_0^2[y_0(t) z_0(t)]] [m_{yy}^{1/2}[y_0(t) z_0(t)]]^T \Delta y_0(t) + \int_0^t d\tau [m_{yy}^{1/2}[y_0(t) z_0(t)]] \\ & \times [\omega_c^2[y_0(t) z_0(t)]] \theta_1[t - \tau; y_0(\tau)] [\omega_c^2[y_0(t) z_0(t)]]^T [m_{yy}^{1/2}[y_0(t) z_0(t)]]^T \Delta y_0(\tau) \\ & + [m_{yy}^{1/2}[y_0(t) z_0(t)]] [\omega_c^2[y_0(t) z_0(t)]] [m_{yy}^{1/2}[y_0(t) z_0(t)]]^T R_1[t; y_0(t)], \end{aligned} \quad (\text{A16})$$

with the MTGLE quantities defined by Eqs. (A11)–(A15).

We conjecture, but have not been able to prove, that Eq. (A16) is exact in the limit of infinitely small amplitude oscillations $y_0(t)$ if the MTGLE quantities are evaluated using the linear response formulas of Sec. V E.

Notice [see Eqs. (A7) and (A9)] that $\mathcal{F}_{y_0}[t; y_0(t)]$ and hence the MTGLE random force is rigorously a functional of the whole trajectory $y_0(\tau)$, $0 \leq \tau \leq t$. Within the linear response model of Sec. V one approximates

$$\mathcal{F}[t; y_0(t)] \cong \mathcal{F}_{0y_0}[t; y_0]_{y_0 = y_0(t)}, \quad (\text{A17})$$

where $\mathcal{F}_{0y_0}[t; y_0]$ is defined in Eq. (A3). Given the linear response approximation of Eq. (B17), the random force depends only on the instantaneous position of the coordinates y_0 rather than on the full trajectory $y_0(\tau)$. Thus within the linear response approximation, the MTGLE random force may be readily modeled by stochastic methods.

The linear response approximation (A17) is exact for common limiting cases like perfectly harmonic solvents, infinitely large solute/solvent mass ratios, etc. Moreover the approximation is valid to second order in smallness. The first order of smallness comes from the fact that the fluctuating force is itself a small quantity relative to the systematic forces in the limit of low temperature. The second order in smallness comes from the fact that $\mathcal{F}[t; y_0(t)]$ and $\mathcal{F}_{0y_0}[t; y_0]_{y_0 = y_0(t)}$ are identical to order $[y_0(t)]^0$.

To reduce Eqs. (A15) to (3.1) we must justify the following three substitutions:

$$\begin{aligned} \langle \mathcal{F}_{y_0} \rangle_{y_0} & \rightarrow \langle \mathcal{F}_{y_0} \rangle_{y_0(t)}, \quad (\text{i}) \\ \omega_c^2[y_0 z_0] - \Omega_0^2[y_0 z_0] & \rightarrow \omega_c^2[y_0 z_0], \quad (\text{ii}) \\ \Delta y_0(t) & \rightarrow y_0(t). \quad (\text{iii}) \end{aligned} \quad (\text{A18})$$

The basis of substitutions (i) and (ii) lies in the physical interpretations of the Einstein frequency $\omega_c[y_0 z_0]$ and the adiabatic frequency $\Omega_0[y_0 z_0]$. By analogy to earlier discussions,¹ the Einstein frequency governs the magnitude of the

restoring force exerted by the solvent on the coordinates y_0 immediately after a slight displacement of these coordinates $\Delta y_0(0)$ from point $y_0(0)$. The adiabatic frequency, in contrast, governs the solvent restoring force an infinitely long time after the displacement Δy_0 . [In practice an infinitely long time is a time of sufficient length (~ 1 ps in simple solvents) to permit the z_0 and q degrees of freedom to fully relax in response to the displacement Δy_0 .]

The fully relaxed restoring force, on physical grounds, must be less than the instantaneous restoring force. In fact one may prove the rigorous inequality

$$\Omega_0[y_0 z_0] < \omega_c[y_0 z_0] \quad (\text{A19})$$

for the case that y_0 represents a single degree of freedom. Additionally if the coordinates y_0 are the Cartesian coordinates of an isolated solute atom in a homogeneous solvent, one may show that $\Omega_0[y_0 z_0]$ is rigorously zero. Our earlier numerical work,¹¹ moreover, suggests that for interacting solutes often

$$\Omega_0[y_0 z_0] \ll \omega_c[y_0 z_0]. \quad (\text{A20})$$

We will assume that Eq. (A20) holds. Then substitution (ii) of Eq. (A18) follows immediately. Also for small amplitude oscillations $y_0(t)$ one has that [use Eq. (A14)]

$$\begin{aligned} \langle \mathcal{F}_{y_0} \rangle_{y_0(t)} & = \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} + \frac{\partial \langle \mathcal{F}_{y_0} \rangle_{y_0}}{\partial y_0^T} \cdot \Delta y_0(t) \\ & = \langle \mathcal{F}_{y_0} \rangle_{y_0(0)} - [m_{yy}^{1/2}[y_0 z_0]] \Omega_0^2[y_0 z_0] \\ & \quad \times [m_{yy}^{1/2}[y_0 z_0]]^T \Delta y_0(t). \end{aligned} \quad (\text{A21})$$

Substitution (i) of Eq. (A.18) follows immediately from Eqs. (A16), (A20), and (A21).

Substitution (iii) holds on time scales sufficiently long that memory of the initial displacement $y_0(0)$ has relaxed away. The time scale in question is the time [1 ps in simple solvents] for decay of the response function $\theta_1[t; y_0]$ to zero.

This may be proven using the identity (analogous to one proven in Sec. VI of Ref. 1)

$$\int_0^\infty [\omega_{c_1}^2 [y_0 z_0]] \theta_1[\tau; y_0] [\omega_{c_1}^2 [y_0 z_0]]^T d\tau \\ = [\omega_{c_1}^2 [y_0 z_0] - \Omega_0^2 [y_0 z_0]].$$

Comparison of Eqs. (A16) and (A22) shows that on time scales long compared to the relaxation time of $\theta_1[t; y_0]$ substitution (iii) of Eq. (A18) is permissible.

Thus we have shown that Eq. (3.1) is a physically realistic model equation of motion for generalized displacements: (i) If the instantaneous solvent restoring force is much greater than the fully relaxed solvent restoring force; (ii) after information about the initial conditions have relaxed away.

APPENDIX B: THE LIOUVILLE OPERATOR L_c TO ORDER $\Delta y_0(t)$

We next give a brief plausibility argument for Eqs. (5.5)–(5.7), the result for the Liouville operator L_c of the constrained solution to order $\Delta y_0(t)$. A more lengthy but rigorous derivation which gives the same result can be made.²⁹

Our argument is based on the fact that to order $\Delta y_0(t)$ iL_c must be of the form

$$iL_c = iL_0 + iL_1 \Delta y_0(t), \quad (B1)$$

where iL_0 , the Liouville operator if $y_0(t)$ is fixed at y_0 , is given by Eq. (5.6) and where iL_1 is independent of $\Delta y_0(t)$.

Thus to establish Eqs. (5.5)–(5.7) we only need to show that

$$iL_1 = \sum_{\alpha=1}^q \left\{ \frac{\partial}{\partial p_{z0\alpha}} \frac{\partial F_{0y_0}^T}{\partial z_{0\alpha}} - \frac{\partial}{\partial z_{0\alpha}} \frac{\partial F_{0y_0}^T}{\partial p_{z0\alpha}} \right\} \\ + \sum_{\alpha=1}^s \sum_{\lambda=1}^{N_\alpha} \left\{ \frac{\partial}{\partial \mathbf{p}_{\lambda\alpha}} \cdot \frac{\partial F_{0y_0}^T}{\partial \mathbf{q}_{\lambda\alpha}} - \frac{\partial}{\partial \mathbf{q}_{\lambda\alpha}} \cdot \frac{\partial F_{0y_0}^T}{\partial \mathbf{p}_{\lambda\alpha}} \right\}. \quad (B2)$$

We will prove Eq. (B2) by considering the special case of a constant displacement, i.e., $\Delta y_0(t) = \Delta y_0$. Since iL_1 is independent of $\Delta y_0(t)$, proof of Eq. (B2) for this special case is sufficient to establish Eqs. (5.5)–(5.7).

We thus assume that the generalized coordinates y_0 are displaced from their initial value y_0 to a new fixed value $y_0 + \Delta y_0$ at $t = 0$, i.e.,

$$y_0(t) = y_0 + \Delta y_0, \quad t > 0. \quad (B3)$$

The assumption of Eq. (B2) leads to simplification since if $\dot{y}_0(t) = 0$, the Hamiltonian K of the constrained solution is independent of the generalized momenta p_{y_0} . Specifically, given Eq. (B3), the Hamiltonian K for $t > 0$ is

$$K = K_0[Q; y_0 + \Delta y_0], \quad t > 0, \quad (B4)$$

where $K_0[Q; y_0]$ is defined by Eq. (5.1).

Given Eq. (B4) it follows that L_c for the case of constant displacements is given by Eq. (5.6) with $K_0[Q; y_0]$ replaced by $K_0[Q; y_0 + \Delta y_0]$. Expanding this result in a power series in Δy_0 yields Eqs. (B1) and (B2) to order Δy_0 .

Thus we have proven Eq. (B2) and hence established Eqs. (5.5)–(5.7).

APPENDIX C: FACTORIZATION OF $f_{CA}^{(0)}[Q; y_0]$

In this Appendix we derive the factorization relation for $f_{CA}^{(0)}[Q; y_0]$ presented in Eq. (6.1) and also prove a number of other results required in Sec. VI. We begin by noting that combining Eqs. (5.1), (5.10), and (6.2) yields the following expression for $f_{CA}^{(0)}[Q; y_0]$:

$$f_{CA}^{(0)}[Q; y_0] = \frac{Z_{CA}^{(0)}[y_0 z_0]}{Z_{CA}^{(0)}[y_0]} \exp[-\beta(p_{z_0}^T m_{zz}^{-1}[y_0 z_0] p_{z_0} \\ + U_{UU}[y_0 z_0])] f_{CA}^{(0)}[p_q q; y_0 z_0]. \quad (C1)$$

Next we consider the phase space pdf $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$ required in Sec. VI. This is defined in terms of $f_{CA}^{(0)}[Q; y_0]$ by

$$f_{CA}^{(0)}[p_{z_0} z_0; y_0] = \int dp_q dq f_{CA}^{(0)}[Q; y_0]. \quad (C2)$$

Since $f_{CA}^{(0)}[Q; y_0]$ is unit normalized [see Eqs. (5.10) and (5.11)], it follows from Eqs. (C1) and (C2) that both $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$ and $f_{CA}^{(0)}[p_q q; y_0 z_0]$ are also unit normalized, i.e.,

$$\int dp_{z_0} dz_0 f_{CA}^{(0)}[p_{z_0} z_0; y_0] = 1, \quad (C3a)$$

$$\int dp_q dq f_{CA}^{(0)}[p_q q; y_0 z_0] = 1. \quad (C3b)$$

Combining Eqs. (C1)–(C3) then yields the following result for $f_{CA}^{(0)}[p_{z_0} z_0; y_0]$:

$$f_{CA}^{(0)}[p_{z_0} z_0; y_0] = \frac{Z_{CA}^{(0)}[y_0 z_0]}{Z_{CA}^{(0)}[y_0]} \\ \times \exp\left[-\frac{\beta}{2}(p_{z_0}^T m_{zz}^{-1}[y_0 z_0] p_{z_0} + U_{UU}[y_0 z_0])\right]. \quad (C4a)$$

We next note that Eqs. (C4a) and (6.4) are identical if we define the solute cavity potential $w_{UU}[y_0 z_0]$ by

$$\exp[-\beta w_{UU}[y_0 z_0]] = Z_{CA}^{(0)}[y_0 z_0]. \quad (C5)$$

Equations (C4a) and (C5) yield

$$f_{CA}^{(0)}[p_{z_0} z_0; y_0] = [Z_{CA}^{(0)}[y_0]]^{-1} \\ \times \exp\left[-\frac{\beta}{2}(p_{z_0}^T m_{zz}^{-1}[y_0 z_0] p_{z_0} \\ + U_{UU}[y_0 z_0] + w_{UU}[y_0 z_0])\right] \quad (C4b)$$

which is identical to Eq. (6.4). Finally comparing Eqs. (C1) and (C4) yields the factorization identity

$$f_{CA}^{(0)}[Q; y_0] = f_{CA}^{(0)}[p_{z_0} z_0; y_0] f_{CA}^{(0)}[p_q q; y_0 z_0]. \quad (C6)$$

Thus we have proven Eq. (6.1).

We next prove Eq. (6.8b). We begin by noting that $\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0}$ may be written as [cf. Eq. (6.8a)]

$$\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0} = \int dp_q dq f_{CA}^{(0)}[p_q q; y_0 z_0] \left[-\frac{\partial K_{VU}}{\partial y_0} \right]. \quad (C8)$$

Next taking the logarithm of Eq. (6.3) and differentiating the result with respect to y_0 yields the following relationship:

$$\beta^{-1} \frac{\partial \ln Z_{CA}^{(0)}[y_0 z_0]}{\partial y_0} = \int dp_q dq \left[- \frac{\partial K_{VU}}{\partial y_0} \right] f_{CA}^{(0)}[p_q q; y_0 z_0]. \quad (C9)$$

Comparing Eqs. (C5), (C7), and (C8) yields

$$\langle \mathcal{F}_{y_0} \rangle_{y_0 z_0} = - \frac{\partial w_{UU}[y_0 z_0]}{\partial y_0} \quad (C10)$$

which is identical to Eq. (6.8b).

¹S. A. Adelman, *Adv. Chem. Phys.* **53**, 61 (1983). Also see references to earlier work cited in this article.

²For recent reviews with many references to earlier work on condensed phase spectroscopic processes see: (a) For liquid state spectroscopic processes D. W. Oxtoby, *Adv. Chem. Phys.* **40**, 1 (1979); (b) For solid state spectroscopic processes, see L. E. Brus and V. E. Bondybey, in *Radiationless Transitions*, edited by S. H. Lin (Academic, New York, 1980).

³For a recent review concerning liquid state energy relaxation processes, with many references to earlier work, see D. W. Oxtoby, *Adv. Chem. Phys.* **51**, 487 (1981).

⁴For some recent experimental studies of liquid solution chemical reaction dynamics see, for example: (a) For photolysis reactions, T. J. Chuang, G. W. Hoffman, and K. B. Eisenthal, *Chem. Phys. Lett.* **25**, 201 (1974); C. A. Langhoff, K. Gnädig, and K. B. Eisenthal, *Chem. Phys.* **46**, 117 (1980); C. A. Langhoff, B. Moore, and M. De Meuse, *J. Am. Chem. Soc.* **104**, 3576 (1982); D. F. Kelley and P. M. Rentzepis, *Chem. Phys. Lett.* **85**, 85 (1982); P. Bado, P. H. Berens, and K. R. Wilson *Proc. Soc. Photo-Opt. Instrum. Eng.* **322**, 230 (1982); (b) For isomerization reactions D. L. Hasha, T. Eguchi, and J. Jonas, *J. Chem. Phys.* **75**, 1571 (1981) and *J. Am. Chem. Soc.* **104**, 2290 (1982); S. P. Velsko and G. R. Fleming, *Chem. Phys.* **65**, 59 (1982) and *J. Chem. Phys.* **76**, 3553 (1982).

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⁹(a) C. L. Brooks III, M. W. Balk, and S. A. Adelman, *J. Chem. Phys.* **79**, 784 (1983); (b) M. W. Balk, C. L. Brooks III, and S. A. Adelman, *J. Chem. Phys.* **79**, 804 (1983).

¹⁰For applications of the MTGLE theory to other important problems in condensed phase chemical kinetics see: (a) M. Olson and S. A. Adelman, *Phys. Rev.* (to be published); (b) H. L. Nguyen and S. A. Adelman, *J. Chem. Phys.* (to be published); (c) R. Stote and S. A. Adelman, *ibid.* (to be published).

¹¹For application of the MTGLE theory (a) to calculation of reagent configuration dependent correlation functions see C. L. Brooks III and S. A. Adelman, *J. Chem. Phys.* **76**, 1007 (1982); (b) to modeling of reagent configuration-dependent correlation functions see *ibid.* **77**, 484 (1982).

¹²The fundamental role played by the solvent frequency spectrum in liquid state chemical reaction dynamics has also been recognized by Wilson and co-workers. See, for example, Fig. 9 of P. Bado, P. H. Berens, J. P. Bergsma, M. H. Coladonto, C. G. Dupery, P. M. Edelsten, J. D. Kahn, and K. R. Wilson, in *Proceedings of the International Conference on Photochemistry and Photobiology*, edited by A. Zewail (Harwood Academic, New York, 1983).

¹³These limiting cases include the case of solutes for which the solute-solvent mass ratio tends to infinity and the case of solutes linearly coupled to perfectly harmonic solvents.

¹⁴The clamping approximation was suggested by the rigorous mathematical operation of chain atom clamping which is MTLE analog of the Mori (Ref. 6) projection process (see Ref. 1).

¹⁵See, for example, the numerical tests of the clamping approximation presented in Ref. 12.

¹⁶An example of this breakdown was given in Ref. 10(b) where the small excursion or linear response model was shown to only crudely describe the very fast initial cage breakout step of the I_2 photolysis process. A solid state example is discussed in the paper of Brus and Bondybey [Ref. 2(b)]. They mention that the rotation of diatomic hydrides in low temperature rare gas matrices is nearly free.

¹⁷For example, for molecular iodine in simple solvents only four of the 36 matrix elements of the response function surfaces are distinct and nonnegligible.

¹⁸For a detailed analysis of the dynamics of molecular vibrations see, for example, E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Spectra* (Dover, New York, 1965).

¹⁹For a quantitative formulation of the concept of a reaction coordinate see R. A. Marcus, *J. Chem. Phys.* **45**, 4493, 4500 (1966) and *J. Chem. Phys.* **45**, 4500 (1968). For related work, see R. A. Marcus, *J. Chem. Phys.* **49**, 2617 (1968). For a recent formulation see W. H. Miller, *J. Chem. Phys.* **72**, 99 (1980).

²⁰Analytic solution is possible within the parabolic well and barrier approximations for the potential of mean force.

²¹Barrier crossing within the Langevin equation framework is treated by H. A. Kramers. See, for example, S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

²²By including a solvent sheath explicitly, extended MTGLE models which should give results of comparable accuracy to full molecular dynamics calculations may be developed. Within the extended models, however, the simple solvation shell picture of the basic models is obscured.

²³See, for example, H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1980).

²⁴These formulas will be presented elsewhere in applications papers.

²⁵The matrix notation is defined as follows: $r_0 = (r_{01}, r_{02}, \dots, r_{0n})$, $p_0 = (p_{01}, p_{02}, \dots, p_{0n}) = (m_1 \dot{r}_{01}, m_2 \dot{r}_{02}, \dots, m_n \dot{r}_{0n})$, $q = (q_{11}, \dots, q_{N_1}, \dots, q_{1S}, \dots, q_{N_S})$, $p_q = (p_{11}, \dots, p_{N_1}, \dots, p_{1S}, \dots, p_{N_S}) = (M_1 \dot{q}_{11}, \dots, M_1 \dot{q}_{N_1}, \dots, M_S \dot{q}_{1S}, \dots, M_S \dot{q}_{N_S})$, $x_0 = (x_{01}, x_{02}, \dots, x_{03n})$, $p_{x_0} = (p_{x_{01}}, p_{x_{02}}, \dots, p_{x_{03n}})$, and

$$m = \begin{pmatrix} m_1 & & & & \\ & m_1 & & & \\ & & m_2 & & \\ & & & \ddots & \\ & & & & m_n \\ & & & & & m_n \\ & & & & & & m_n \end{pmatrix}.$$

²⁶Equation (2.5) may be readily derived from the results presented in Ref. 23, Chap. 1.

²⁷All matrix square roots taken in this paper will be evaluated by the Choleski prescription as described in E. Bodewig, *Matrix Calculus* (North-Holland, Amsterdam, 1956), Part I.

²⁸See the derivation of Eq. (6.36) given in Ref. 1.

²⁹A rigorous derivation of the form of L_c may be made by following the method of derivation of the Liouville equation from Hamilton's equations for the case of unconstrained dynamics given in Sec. IV B of Ref. 1.

³⁰An analysis shows that Eq. (5.16) holds exactly or approximately if y_0 = internal molecular coordinates, z_0 = center of mass and orientational coordinates; y_0 = one set of normal modes, z_0 = remaining normal modes plus center of mass and orientational coordinates; y_0 = reaction coordinate, and z_0 = other internal coordinates and center of mass and orientational coordinates.